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A MULTIPARAMETER OIL POLLUTION SOURCE IDENTIFICATION SYSTEM

John W. Miller

Phillips Petroleum Company

Prepared for:

Environmental Protection Agency

July 1973

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A MULTIPARAMETER OIL POLLUTION SOURCE IDENTIFICATION SYSTEM

By

John W. Miller

Contract No. 68-01-0059
Project 15080 HDJ

Project Officer

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ABSTRACT

The feasibility of oil pollution source identification is demonstrated on eighty crude oils from the world's major oil fields. Measurements of fifteen diagnostic parameters were made on the 600^+F fraction of the crude oil samples. Of the fifteen parameters studied it was demonstrated that six were sufficient to distinguish among the crude oils. These parameters are carbon and sulfur isotopic composition, sulfur, nitrogen, vanadium and nickel contents. A hydrocarbon gas chromatographic profile was also diagnostic for identification but its usefulness was reduced for aged samples by the effect of weathering. The other parameters studied were the saturate, aromatic and asphaltic contents and the carbon isotopic composition of each of these fractions, the n-paraffin distribution (odd-even predominance curves) and the sulfur gas chromatographic profile. The influence of weathering on the parameters was studied.

A statistical procedure based on multivariate normal analysis was developed to compare an unknown with a data library and to give an unbiased match of the unknown with a known based on the precision of the measurement methods.

This report was submitted by Research and Development Department, Phillips Petroleum Company, Bartlesville, Oklahoma 74004 in fulfillment of Project Number 15080 HDJ, Contract Number 68-01-0059 under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. The feasibility of oil pollution source identification has been demonstrated on eighty crude oils from the world's major oil fields. Measurements of 15 diagnostic parameters were made on the 600^{+}F fraction of the crude oil samples. The parameters are:

   1. Carbon Isotopic Composition
   2. Sulfur Content
   3. Nitrogen Content
   4. Vanadium Content
   5. Nickel Content
   6. Sulfur Isotopic Composition
   7. Hydrocarbon GLC Profile
   8. Sulfur GLC Profile
   9. Saturate Content
   10. Aromatic Content
   11. Asphaltic Content
   12. Odd-Even Predominance Curves
   13. Carbon Isotopic Composition-Saturates
   14. Carbon Isotopic Composition-Aromatics
   15. Carbon Isotopic Composition-Asphaltics

   A multivariate statistical procedure was developed and tested to match the 15 parameters of an "unknown" with those of each 600^{+}F fraction from the crude oils. All 15 parameters were not required for positive identification; the first six listed in (1) above were sufficient to distinguish uniquely among 48 sources.

2. Our outdoor weathering studies demonstrated that of the 15 diagnostic parameters only hydrocarbon GLC profile and saturate, aromatic and asphaltic contents were affected by weathering. The change of the value of these four parameters was dependent upon the length of weathering time (maximum 49 days).

3. **Sulfur isotopic composition is an important identification parameter by virtue of the wide range of its values and its stability to weathering that were established in this study.**

SECTION II

RECOMMENDATIONS

1. It is recommended that the variations in the values of the proposed identification parameters that will occur in the normal course of oil production be established on several major commercial crude oil sources.
2. The proposed multiparameter identification system should be tested on naturally-weathered crude oils to demonstrate its validity.
3. It is recommended that the feasibility of this crude oil identification system be established for other petroleum products such as fuel oils and refined products that are "persistent" in an aqueous environment.
4. An extension of the present studies on sulfur gas chromatographic profile and sulfur isotopic composition is recommended with the objective to reduce their measurements to a routine procedure.

SECTION III

INTRODUCTION

The expanded movement of petroleum by water transport to meet existing and predicted world and U.S. energy demands will increase the accidental or deliberate discharge of persistent oils into the waterways of the world. In U.S. waters in 1971 there were 8,736 spills of oil and other polluting substances as reported by the U.S. Coast Guard.[1] Large spills that resulted from tank rupture and collisions accounted for 40% of the volume spilled (3,537,343 gallons) but only 1.5% of the spill incidents. The source of these catastrophic spills is readily determined. However, of major concern are the large number of smaller spills (2,353), the source of which is unknown. The identification of these spills to establish liability presents a difficult problem to both the law enforcement and the scientific communities. Ideally, the basis for source identification should stand up in legal proceedings without the benefit of circumstantial evidence.

Two general approaches to the identification problem are recognized: passive tagging and active tagging. Passive tagging is based on the properties and constituents indigenous to petroleum and assumes that these properties are sufficiently diverse to distinguish among the large number of crude oil sources. Active tagging is based on the deliberate addition of coded materials to petroleum at each point of liability transfer. The deliberately added materials are chosen so as to be easily measured. The selection of either passive or active tagging depends on an evaluation of objectives and their costs. Whether the objective is to assess liability from an enforcement viewpoint or simply to eliminate one's commercial oil from suspicion must be determined.

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The requirements for active tagging and an illustration of its application are described by Melpar Corporation.[2] The application of magnetic particles to active tagging has been disclosed recently.[3] Although active tagging appears attractive from the measurement point of view, the technical problem of homogeneously blending a relatively few parts per million of coded material into a tanker shipment of crude oil is difficult and would be costly on a worldwide basis. Crude oil is not a uniform material but varies in viscosity from a water-like material to a solid at ambient temperatures depending upon its source. Often, heated-transport facilities are necessary to permit crude oil to be moved. The number of codes required for active tagging is large and the bookkeeping task is not insignificant. It appears that all petroleum transporters would be burdened with the need to tag their cargos to establish liability against a few offenders.

Passive tagging is implemented by the analytical determination of characteristic chemical and physical properties (parameters) of a unknown crude oil residue. These measured parameters are often referred to collectively as "fingerprints" and are compared either with those from a number of suspected sources or with those from a library of all potential sources to identify the unknown. Since the sample itself provides all the evidence for identification, changes which occur in the composition of a crude oil when it is spilled into the environment must be considered. These changes are a result of evaporation, microbial degradation, photolysis, oxidation, dissolution and adsorption and are referred to collectively as "weathering". The most important short-term weathering processes of water-borne oils are evaporative and dissolution losses, which occur at various rates dependent upon environmental conditions (wind velocity and turbulence, temperature of air and water, rate of spill spread, wave action and type of water, fresh or saline). Therefore, any passive tagging system must reduce all petroleum samples, i.e., weathered and unweathered, to a common base for measurement of the indigenous constituents to eliminate or at least minimize the weathering effects. A convenient common base is a distillation bottoms, the properties of which form a basis for comparison.

Passive tagging is often more successful in elimination of suspect sources than in positive identification of an unknown. Therefore, the strength of any passive system will be determined by its ability to identify an unknown uniquely with respect to source.

The Western Oil and Gas Association has developed a tentative method for comparison of unknown petroleum pollutants with known sources based on five measured parameters: sulfur, nitrogen, vanadium and nickel contents and gas chromatography.[4] The success of this comparison method is not known. A wide variation in the values for these parameters exists among crude oils from various sources. In cases where the differences between the known sources are large, this tentative method is adequate to identify a pollutant. If two or more known sources are equivalent within the repeatability of the measurement methods, unambiguous identification is not possible and circumstantial evidence must be considered in the final decision. To strengthen the potential of this tentative method of comparison a number of additional parameters could be considered. Adlard[5] reviewed those identification parameters that have been suggested in the open literature, i.e., infrared spectroscopy, ultraviolet fluorescence spectroscopy and chromatographic techniques. Up to this point no one identification parameter or collection of parameters has been shown to be superior to the others. The particular combination of parameters depends upon the facilities available and the expenditure which is justified to identify an unknown sample.

SECTION IV

OBJECTIVES

The objective of the study described in this report was to develop and test the feasibility of a multiparameter oil pollution source identification system on a worldwide basis. The system studied extended the Western Oil and Gas Association method[4] to include ten additional parameters.

The economic value of a petroleum source depends upon the gross physical and chemical properties of the crude oil. A large library of such data for commercial crude oils exists in the literature and within petroleum industry files and new sources are evaluated continuously on this basis. In general, however, these compositional variables are modified by weathering and are not suitable for identification of an unknown pollutant.

The measured parameters included in this feasibility study were selected on the basis of our experience with comparison techniques for the identification of crude oils with respect to geologic source-rock origin.[6] These comparison techniques were based on an understanding of petroleum genesis, the chemical and physical processes that occur during the migration and accumulation of petroleum in reservoirs, and the changes that occur during weathering. Stability to weathering must be evaluated on the basis of changes in real samples rather than on the basis of changes that are possible with isolated components or compounds[2] which comprise crude oil. The essential requirement is that an identification parameter be stable for a few days to several weeks. Stability is defined operationally as no statistically significant change in the selected parameter.

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If the unknown sample is suspected of being non-representative of the original water-borne oil pollutant, i.e., that the isolated pollutant is contaminated with components from the water or mixed with a second oil or other organic material, the analyst must provide guidance on the interpretation of the data. The ability of the analyst to obtain a sufficient quantity of a representative oil pollutant is a practical consideration not to be ignored.

The development of a system for oil pollution source identification was planned in five phases. Phase I constituted the installation and evaluation of initial analytical procedures while Phase II established an identification feasibility of this approach for North and South America crude oils. Phase III extended this identification feasibility to eastern hemisphere crude oils. Phase IV provided additional parameters to improve the reliability of this approach. Phase V extended the identification scheme to include two additional parameters, sulfur isotope ratios and sulfur gas chromatographic profile.

Practically, Phases I, II and III were conducted concurrently to constitute a study that demonstrated the feasibility of an identification system based on the measurement of carbon isotopic composition in addition to the five parameters recommended by the Western Oil and Gas Association: sulfur, nitrogen, vanadium and nickel contents and the hydrocarbon gas chromatographic profile of simulated-weathered crude oil residues. The crude oils that were used are representative of the major sources of water-transported oils. Then, further characterizations were made using additional parameters in Phase IV by fractionating the crude oil residues into three portions: saturates, aromatics and asphaltics. The carbon isotopic composition was measured on each fraction. The normal paraffins were removed from the saturates fraction and their carbon number distribution was measured. The final portion of the work (Phase V) added the measurement of sulfur isotopic composition and sulfur gas chromatographic profile. The identification potential was strengthened with these added parameters. The combination of these 15 parameters into smaller groups for different degrees of identification potential was also investigated.

The major tasks necessary to achieve the objectives of this study were:

1. Select identification parameters based on experience in crude oil correlation studies.
2. Install and evaluate necessary analytical procedures to measure these parameters.
3. Select crude oils that represent significant worldwide sources and measure the parameters of these oils.
4. Validate the parameter selection on the basis of the variation in parameter values observed for these oils.
5. Develop comparison techniques to match measured parameters for a known and unknown crude oil on an unbiased basis.
6. Evaluate different combinations of parameters with respect to their ability to distinguish among crude oil sources using the comparison techniques developed.
7. Test the influence of weathering on the measured parameters and their identification potential.

SECTION V

CRUDE OIL SOURCES

The crude oils that were included in this study were selected on the basis of the facts discussed in the following paragraphs.

The increased demand for petroleum products in the United States is being met by increased imports of both crude oil and products. Preliminary information for 1972 reported by the American Petroleum Institute (API)[7,8] indicates that crude oil imports were up 30% and product imports up 9% over 1971 levels. Crude oil imports in 1972 amounted to an average of 2,189,000 barrels per day (b/d) with 69% of the 508,000 b/d increase coming east of the Rockies, an area that accounted for 1,515,000 b/d imports. Every indication points to significant increases each year in crude oil imports. Practically all the growth must come from sources in the Eastern Hemisphere.[9] The origin by country of these imports in 1970, 1971, and 1972 is summarized in Table 1.[8] All the areas except South America showed an increase in their imports into the United States with the Middle East and Africa increasing their share of the total at the expense of Canada and South America. The dependence upon the Eastern Hemisphere for increased sources of crude oil imports means that this area and especially the Middle East around the Persian Gulf will become a predominate source of water-transported crude oil imports in future years.

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TABLE 1

ORIGIN OF CRUDE OIL IMPORTS INTO UNITED STATES - 1970, 1971, 1972

	1970		1971		1972*	
	1,000 b/d	% Total	1,000 b/d	% Total	1,000 b/d	% Total
Bolivia	2	0.2	2	0.1	-	-
Columbia	20	1.5	9	0.5	1	-
Chile	-	-	1	0.1	-	-
Trinidad	-	-	-	-	18	0.8
Venezuela	268	20.2	303	18.0	253	11.6
South American Total	291	22.0	315	18.7	272	12.4
Algeria	6	0.5	13	0.8	78	3.6
Angola	-	-	4	0.2	13	0.6
Egypt	21	1.6	19	1.1	7	0.3
Libya	47	3.5	53	3.2	137	6.3
Tunisia	-	-	-	-	6	0.3
Nigeria	48	3.6	95	5.7	231	10.6
Africa Total	122	9.2	184	11.0	472	21.6
Kuwait	33	2.5	29	1.7	31	1.4
Saudi Arabia	40	3.0	115	6.8	166	7.6
Iran	33	2.5	106	6.3	126	5.8
Iraq	-	-	11	0.7	3	0.1
Qatar	-	-	-	-	4	0.2
Abu Dhabi (United Arab Emirates)	63	4.8	80	4.8	119	5.4
Middle East Total	169	12.8	341	20.3	449	20.5
Canada	672	50.8	721	42.9	835	38.1
Far East	70	5.3	117	7.0	161	7.4
Total Crude	1,324	-	1,681	-	2,189	-

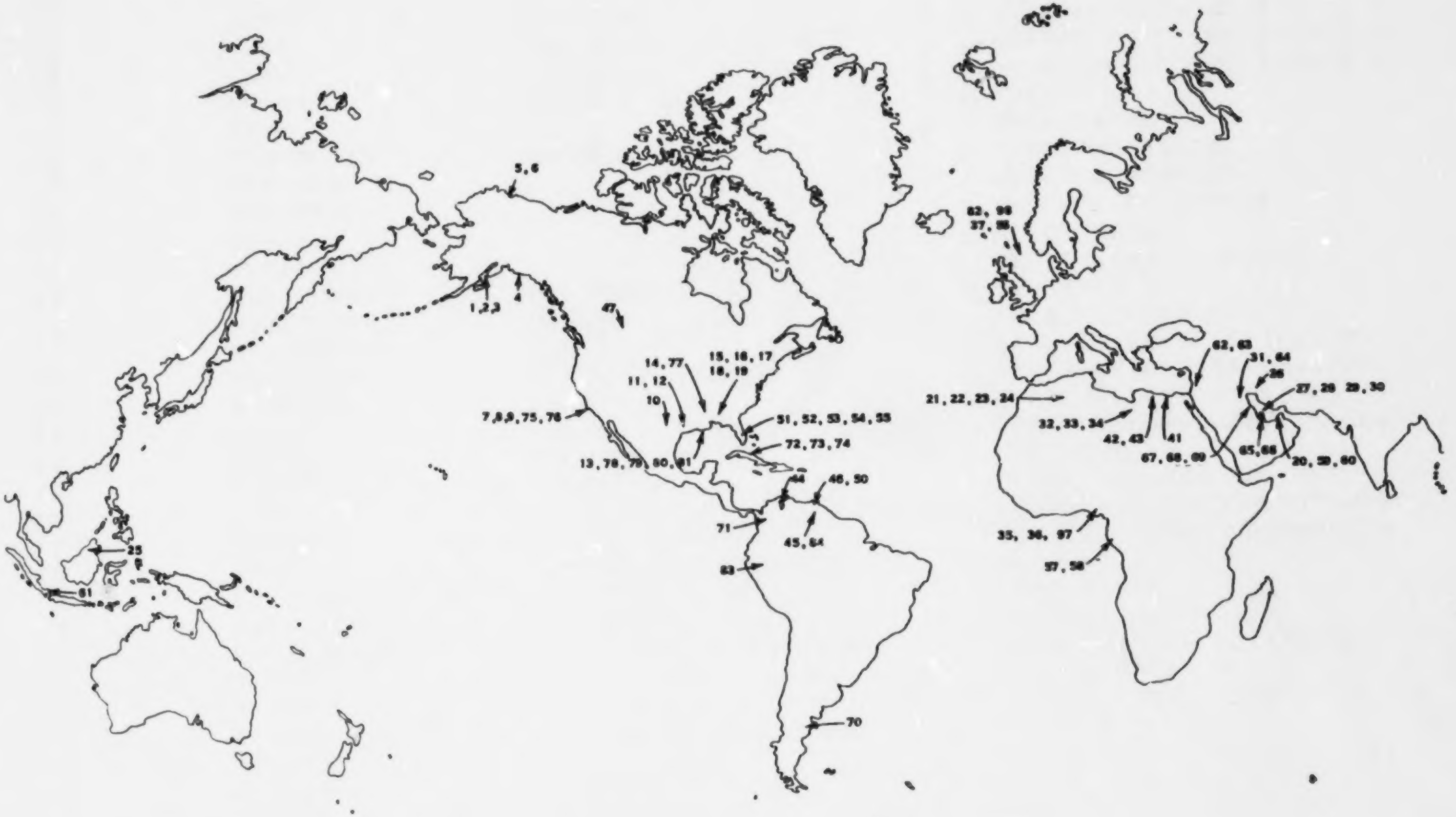
*1972 data are preliminary

New domestic sources of crude oil that will become of increased importance to supply energy demands are located in areas where water pollution is of great concern. Namely, offshore United States in the Gulf of Mexico, especially Louisiana, and the Pacific Ocean between the Gulf of Alaska and the Northwest states and California. The latter ocean area will be crossed with tankers delivering primarily North Slope Alaskan crude oil to United States refineries. The crude oil will cross Alaska through a proposed pipeline. Offshore Louisiana in the deeper waters is in an area of high production potential and will be explored when acreage and equipment become available. As the drilling and production activities grow, the oil pollution potential will increase in the Gulf Coast waters.

Many California crude oils are significantly different in properties from typical Mid-continent or Pennsylvanian crude oils. California crude oils have a relatively high nitrogen and naphthenic acid content and low saturate and normal paraffin content. Their unique characteristics should be considered in any worldwide identification system.

With these facts in mind, representative crude oils were selected on a worldwide basis for this feasibility study of multiparameter source identification systems. The geographic distribution of the selected crude oils is shown in Figure 1. The crude oil sources are identified in numerical order in Table 2 and alphabetically by country in Table 3.

In addition to selection of crude oils from the major producing areas such as Venezuela, offshore Louisiana, Nigeria, Libya, and Saudia Arabia, crude oils were selected from different producing formations in the same field and from the same field at different times. The former is typified by the three Iranian crude oils (Nos. 28,29,30) from three zones in the offshore Rakhsh field and the latter by samples from Nigeria (Nos. 35 and 97). Also included in the representative crude oil samples are two sets of samples from different fields within the same geologic basin: those from the Interior Salt Dome Basin of Mississippi (Nos. 15-19) and the South Florida Basin (Nos. 51-55). This selection of crude oils will allow any identification system to be tested under several realistic situations.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27, 28 29, 30
65, 66
20, 59, 60
35, 36, 97
57, 58

FIGURE 1 - GEOGRAPHICAL DISTRIBUTION OF CRUDE OIL SOURCES

TABLE 2

CRUDE OIL SOURCES IDENTIFICATION BY NUMBER

CRUDE OIL NO.	COUNTRY/ STATE	COUNTY OR REGION	FIELD
1	ALASKA	COOK INLET	MID. GROUND SHOAL-MGS175
2	ALASKA	COOK INLET	MCARTHUR RIVER-MCARTHUR
3	ALASKA	COOK INLET	TRADING BAY-TYONEK ST175
4	ALASKA	GULF OF ALASKA SHORE	KATALLA NO. 1
5	ALASKA	NORTH SLOPE	PRUDHOE BAY - WELL NO. 1
6	ALASKA	NORTH SLOPE	W. KUPARUK - W-3
7	CALIFORNIA	OFF SHORE ST BARBARA	CALIF ST. WELLS 1,2,3,4
8	CALIFORNIA	LOS ANGELES CO.	WILMINGTON
9	CALIFORNIA	ST BARBARA CO.	GATO RIDGE
10	TEXAS	YOAKUM & GAINES CO.	WASSON
11	TEXAS	NUECES CO.	TURKEY CREEK - KENNEDY B
12	TEXAS	BRAZORIA CO.	CHOCOLATE BAYOU GARDINER
13	LOUISIANA	TIMBALIER OFF SHORE	BLOCKS 21 AND 28
14	LOUISIANA	JACKSON PARISH	KELLEY B
15	MISSISSIP	WAYNE	E.YEL CREEK-HUMBLE 2 ROE
16	MISSISSIP	WAYNE	W.YEL CREEK-AM E&D #1
17	MISSISSIP	CLARK	NANCY-PLACID #1 MENASCO
18	MISSISSIP	JONES	POOL CREEK-EL ERICKSON
19	MISSISSIP	JASPER	WEST HEIDELBERG-GULF
20	ABU DHABI	OFFSHORE	ABU ARAB A
21	ALGERIA		GASSI TOUIL (UPPER)
22	ALGERIA		NEZLA NORD
23	ALGERIA		RHOURDI EL BAGUEL
24	ALGERIA		HASSI-MESSAOUND
25	INDONESIA	BRUNET	JERUDONG FIELD
26	IRAN		GACH SARAN
27	KUWAIT	NEUTRAL ZONE	KHAFJI
28	IRAN	OFFSHORE	RAKHSH-WELL ARK 1-ZONE S
29	IRAN	OFFSHORE	RAKHSH-WELL ARK 1-ZONE A
30	IRAN	OFFSHORE	RAKHSH-WELL ARK 1-ZONE M
31	KUWAIT	NEUTRAL ZONE	WAFRA
32	LIBYA		HOFRA

TABLE 2 (CONTD.)

CRUDE OIL NO.	COUNTRY/ STATE	COUNTY OR REGION	FIELD
33	LIBYA	CYRENAICA	KHUFF
34	LIBYA		AMOSCAS BEIDE
35	NIGERIA		EBOCHA
36	NIGERIA		AGIOS
37	NORWAY	NORTH SEA	EKOFISK-WELL 2-4-5X,DIS4
41	UN ARAB RP		ALAMEIN-WELL #1X
42	UN ARAB RP		UMBARKA-WELL 1A
43	UN ARAB RP		GHROUD FIELD-WELL 1-X
44	VENEZUELA	LAKE MARACAIBO	BLOCK 17-WELL SDC-2
45	VENEZUELA	MONAGAS	MORICHAL
46	VENEZUELA	QUIRIQUIRE	
47	CANADA	ALBERTA	SOUTH SWAN HILLS
50	VENEZUELA	ANZOATEQUI	OSCUROTE NOTRE
51	FLOPIDA	COLLIER	LAKE TRAFFORD FIELD
52	FLORIDA	COLLIER	SUNNILAND FIELD
53	FLORIDA	HENDRY	FELDA FIELD
54	FLORIDA	LEE	LEHEIGH FIELD
55	FLORIDA	HENDRY-LEE	WEST FELDA FIELD
56	NORWAY	NORTH SEA	EKOFISK CRUDE # 2
57	GABON		BATANGA
58	GABON		TEHENQUE
59	ABU DHABI		BU HASA I
60	ABU DHABI		MURBAN-BAB-BU-HASA
61	INDONESIA		PENATANG
62	ISRAEL		HELETZ
63	ISRAEL		KOKHAV
64	KUWAIT		MAGWA-AHMADI
65	QATOR		IDD-EL-SHARGI
66	QATOR		MAYDAN-MAHZAN
67	SAUDI ARAB		GHAWAR (HARADH)
68	SAUDI ARAB		QATIF
69	SAUDI ARAB		SAFANIYA

TABLE 2 (CONTD.)

CRUDE OIL NO.	COUNTRY/ STATE	COUNTY OR REGION	FIELD
70	ARGENTINA		CERRO DRAGON-CANADON GR.
71	COLOMBIA		PAYOA
72	CUBA		BACURANOO-CRUZ VERDE
73	CUBA		DOS ESTRELLAS (JATIBON.)
74	CUBA		SANTA MARIE DEL MAR
75	CALIFORNIA	ST. BARBARA	LOMPAC
76	CALIFORNIA	ST. BARBARA	SANTA MARIA VALLEY
77	LOUISIANA	CLAIBORNE PARISH	COLQUITT
78	LOUISIANA	OFFSHORE	DELTA WEST (BLOCK 27)
79	LOUISIANA	OFFSHORE	DELTA WEST (BLOCK 41)
80	LOUISIANA	OFFSHORE	EUGENE ISLAND (BLK 276)
81	LOUISIANA	OFFSHORE	SHIP SHOAL (BLOCK 176)
82	NORWAY		WEST EKOFISK
83	VENEZUELA	MONAGAS	PIPELINE CRUDE
84	ECUADOR		GULF COMPOSITE

TABLE 3

CRUDE OIL SOURCES - ALPHABETIC BY COUNTRY

CRUDE OIL NO.	COUNTRY/ STATE	COUNTY OR REGION	FIELD
60	ABU DHABI		MURBAN-BAB-BU-HASA
59	ABU DHABI		BU HASA I
20	ABU DHABI	OFFSHORE	ABU ARAB A
2	ALASKA	COOK INLET	MCARTHUR RIVER-MCARTHUR
1	ALASKA	COOK INLET	MID. GROUND SHOAL-MGS175
3	ALASKA	COOK INLET	TRADING BAY-TYONEK ST175
4	ALASKA	GULF OF ALASKA SHORE	KATALLA NO. 1
5	ALASKA	NORTH SLOPE	PRUDHOE BAY - WELL NO. 1
6	ALASKA	NORTH SLOPE	W. KUPARUK - W-3
21	ALGERIA		GASSI TOUIL (UPPER)
22	ALGERIA		NEZLA NORD
24	ALGERIA		HASSI-MESSAOUNU
23	ALGERIA		RHOURDI EL BAGUEL
70	ARGENTINA		CERRO DRAGON-CANADON GR.
8	CALIFORNIA	LOS ANGELES CO.	WILMINGTON
7	CALIFORNIA	OFF SHORE ST BARBARA	CALIF ST. WELLS 1,2,3,4
9	CALIFORNIA	ST BARBARA CO.	GATO RIDGE
75	CALIFORNIA	ST. BARBARA	LOMPAC
76	CALIFORNIA	ST. BARBARA	SANTA MARIA VALLEY
47	CANADA	ALBERTA	SOUTH SWAN HILLS
71	COLOMBIA		PAYOA
72	CUBA		BACURANOO-CRUZ VERDE
74	CUBA		SANTA MARIE DEL MAR
73	CUBA		DOS ESTRELLAS (JATIBON.)
84	ECUADOR		GULF COMPOSITE
52	FLORIDA	COLLIER	SUNNILAND FIELD
51	FLORIDA	COLLIER	LAKE TRAFFORD FIELD
53	FLORIDA	HENDRY	FELDA FIELD
55	FLORIDA	HENDRY-LEE	WEST FELDA FIELD
54	FLORIDA	LEE	LEHEIGH FIELD
57	GABON		BATANGA
58	GABON		TEHENQUE

TABLE 3 (CONTD.)

CRUDE OIL NO.	COUNTRY/ STATE	COUNTY OR REGION	FIELD
61	INDONESIA		PENATANG
25	INDONESIA	BRUNET	JERUDONG FIELD
26	IRAN		GACH SARAN
30	IRAN	OFFSHORE	RAKHSH-WELL ARK 1-ZONE M
29	IRAN	OFFSHORE	RAKHSH-WELL ARK 1-ZONE A
28	IRAN	OFFSHORE	RAKHSH-WELL ARK 1-ZONE S
63	ISRAEL		KOKHAV
62	ISRAEL		HELETZ
64	KUWAIT		MAGWA-AHMADI
27	KUWAIT	NEUTRAL ZONE	KHAFJI
31	KUWAIT	NEUTRAL ZONE	WAFRA
34	LIBYA		AMOSCAS BEIDE
32	LIBYA		HOFRA
33	LIBYA	CYRENAICA	KHUFF
77	LOUISIANA	CLAIBORNE PARISH	COLQUITT
14	LOUISIANA	JACKSON PARISH	KELLEY B
78	LOUISIANA	OFFSHORE	DELTA WEST (BLOCK 27)
80	LOUISIANA	OFFSHORE	EUGENE ISLAND (BLK 276)
79	LOUISIANA	OFFSHORE	DELTA WEST (BLOCK 41)
81	LOUISIANA	OFFSHORE	SHIP SHOAL (BLOCK 176)
13	LOUISIANA	TIMBALIER OFF SHORE	BLOCKS 21 AND 28
17	MISSISSIP	CLARK	NANCY-PLACID #1 MENASCO
19	MISSISSIP	JASPER	WEST HEIDELBERG-GULF
18	MISSISSIP	JONES	POOL CREEK-EL ERICKSON
16	MISSISSIP	WAYNE	W.YEL CREEK-AM E&D #1
15	MISSISSIP	WAYNE	E.YEL CREEK-HUMBLE 2 ROE
36	NIGERIA		AGIOS
35	NIGERIA		EBOCHA
82	NORWAY		WEST EKOFISK
56	NORWAY	NORTH SEA	EKOFISK CRUDE # 2
37	NORWAY	NORTH SEA	EKOFISK-WELL 2-4-5X,DIS4
66	QATOR		MAYDAN-MAHZAN

TABLE 3 (CONTD.)

CRUDE OIL NO.	COUNTRY/ STATE	COUNTY OR REGION	FIELD
65	QATOR		IDD-EL-SHARGI
69	SAUDI ARAB		SAFANIYA
68	SAUDI ARAB		QATIF
67	SAUDI ARAB		GHAWAR (HARADH)
12	TEXAS	BRAZORIA CO.	CHOCOLATE BAYOU GARDINER
11	TEXAS	NUECES CO.	TURKEY CREEK - KENNEDY B
10	TEXAS	YOAKUM & GAINES CO.	WASSON
41	UN ARAB RP		ALAMEIN-WELL #1X
42	UN ARAB RP		UMBARKA-WELL 1A
43	UN ARAB RP		GHROUD FIELD-WELL 1-X
50	VENEZUELA	ANZOATEQUI	OSCUROTE NOTRE
44	VENEZUELA	LAKE MARACAIBO	BLOCK 17-WELL SDC-2
45	VENEZUELA	MONAGAS	MORICHAL
46	VENEZUELA	QUIRIQUIRE	
83	VENEZUELA	MONAGAS	PIPELINE CRUDE

SECTION VI

MEASUREMENT OF PARAMETERS

Each of the crude oils and weathered samples were reduced to a "topped" residue using a vacuum distillation procedure before the identification parameters were measured. The residues have an initial boiling point above 600°F and will be referred to as the "600^{+}F bottoms" or merely "bottoms". The possibility of thermal cracking is minimized by limiting the distillation temperature to about 100°C (212°F) and by reducing the duration of heating. The vacuum distillation or vacuum flash procedure is described in detail in Appendix A.

The crude oil bottoms are analyzed for total sulfur using ASTM D 1552, a high temperature combustion procedure that converts the organic sulfur to sulfur dioxide, which is measured by an iodometric titration. Total nitrogen is measured by a high temperature oxidative combustion procedure to produce elemental nitrogen which is determined by thermal conductivity. The details of the procedure are in Appendix B. The vanadium and nickel contents are measured on a single portion of the bottoms, which is decomposed by incineration with sulfur to prevent loss of volatile metalloporphyrins.[10] The resulting metal sulfides are analyzed for vanadium and nickel content by atomic absorption spectrometry in nitrogen oxide-acetylene and oxygen-hydrogen flames, respectively.

The hydrocarbon gas chromatographic (GLC) profile on each bottoms is obtained by a procedure equivalent to the dual column technique outlined by the Institute of Petroleum.[11] The bottoms are flash vaporized into a gas-liquid chromatographic column, where the components are separated by increasing boiling point. The procedural details are described in Appendix C. Interpretation of the chromatograms is discussed in Section VII.

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The carbon isotopic composition, i.e., the proportion of carbon present as the stable isotope carbon-13 versus the predominant isotope carbon-12 and commonly referred to as the carbon isotopic "ratio" or $\delta^{13}C$ (pronounced "del C-13"), is measured by means of an isotope ratio mass spectrometer. This type of mass spectrometer makes precise isotope ratio measurements by the simultaneous collection of ions composed of either the major or the minor isotope.[12] A schematic diagram and description of the instrument used for this study are in Appendix D. Carbon isotopes are measured on carbon dioxide, which is prepared from the crude oil bottoms by their combustion in an oxygen atmosphere.[13] The over-all standard deviation of the carbon isotopic composition measurement is 0.1 per mil or better (see Section VII, Equation 5 for definition).

The sulfur isotopic composition, i.e., the proportion of sulfur present as the stable isotope sulfur-34 versus the predominant isotope sulfur-32 (sulfur isotope ratio or $\delta^{34}S$), of the 600^{+}F bottoms is measured on sulfur dioxide with the isotope ratio mass spectrometer (Appendix D). The organic sulfur in the bottoms is reduced by hydrogenation to hydrogen sulfide and recovered quantitatively as solid silver sulfide, Ag_2S. This procedure is an alternate means to measure the total sulfur content of the bottoms and serves as a check on the more rapid ASTM procedure. Roasting of the silver sulfide with cupric oxide forms sulfur dioxide, which is purified before mass spectrometric measurement. These reactions are summarized below:

$$\text{Organic Sulfur} \xrightarrow{H_2} [H_2S] \xrightarrow{Ag^+} \underline{Ag_2S} \qquad (1)$$

$$Ag_2S \xrightarrow[\Delta]{CuO} SO_2 \qquad (2)$$

This is referred to as the reductive approach to sulfur isotope ratios. The detailed procedures to accomplish these conversions are described in Appendices E and F.

An oxidative approach was also used on a few 600^+F bottoms. This embodies combustion of the samples in oxygen to form barium sulfate, which is converted quantitatively to silver sulfide as follows:

$$\text{Organic Sulfur} \xrightarrow[\Delta]{O_2} [SO_2] \xrightarrow[H_2O]{H_2O_2} \underset{\text{aq.}}{[H_2SO_4]} \xrightarrow{Ba^{++}} \underline{BaSO_4} \tag{3}$$

$$BaSO_4 \xrightarrow[H_3PO_2]{HI} [H_2S] \xrightarrow{Cd^{++}} \underline{CdS} \xrightarrow{Ag^+} \underline{Ag_2S} \tag{4}$$

Reaction (3) also can serve as an additional procedure to determine total sulfur but is much less convenient. The procedures to conduct the oxidative approach are described in Appendices G and H.

The sulfur GLC profiles[14] are obtained in a manner analogous to the GLC profiles except that a sulfur-selective flame photometric detector (FPD) is used to determine the approximate boiling point distribution of the sulfur-containing components of the 600^+F bottoms. The exact operating instructions are in Appendix I.

Further characterization of each crude oil bottoms is accomplished by measurement of seven additional parameters. The bottoms are fractionated by liquid-solid adsorption chromatography over silica gel into three portions: saturates, aromatics, and asphaltics. In general, the material recovery from the silica gel is greater than 85%; samples giving recovery less than this should be re-run. The detailed procedure is described in Appendix J. The carbon isotopic composition is determined on each fraction as previously described (Appendix D).

The saturates portion is treated to isolate the n-paraffins (straight-chain saturated hydrocarbons) by urea adduction. The carbon number distribution from C_{13} to C_{38} of the n-paraffins is measured by gas chromatography and is expressed as a normalized weight per cent of each n-paraffin present. This composition does not represent their concentration in the crude oil bottoms or the saturate fraction. The significance in the n-paraffins is in their relative concentrations to one another and not their absolute concentration in the original sample. A complete description of these two procedures is in Appendices K and L.

The data obtained by these measurement procedures and their interpretation with respect to source identification are discussed in Section VII.

SECTION VII

RESULTS AND DISCUSSION

Each of the 80 crude oils selected for study were characterized by the sequence of steps illustrated schematically in Figure 2 and the procedures outlined in Section VI.

In any passive tagging approach, the comparison of parameters or "fingerprints" must be made on a basis that eliminates or, at least, minimizes the influence of weathering on the measured parameters. In the earlier stages of weathering most of the changes in the characteristics of the oil are due to the effects of evaporation and dissolution of the lighter components of the crude oil. The preparation of distillation bottoms with an initial boiling point above 518°F is expected to eliminate the effects of evaporative weathering.[15] Thus, the preparation of the "600^{+}F bottoms" provides a residue that can serve as a convenient base for the measurement and comparison of selected parameters. The 600^{+}F initial boiling point used for this work is intermediate between that chosen by the Western Oil and Gas Association (540^{+}F bottoms)[4] and the Institute of Petroleum (649^{+}F bottoms).[5]

The first operation in the sequence of steps outlined in Figure 2 is the preparation of the "600^{+}F bottoms" or merely "bottoms". Since thermal cracking of crude oils can occur at temperatures as low as 150°C and this cracking could result in a modification of the indigenous properties of the oil, it is necessary to limit the temperature and duration of the distillation. The method chosen utilizes a vacuum distillation, which is more nearly a vacuum flask, in which the operation is carried out at 101°C and 0.15 mm Hg pressure.

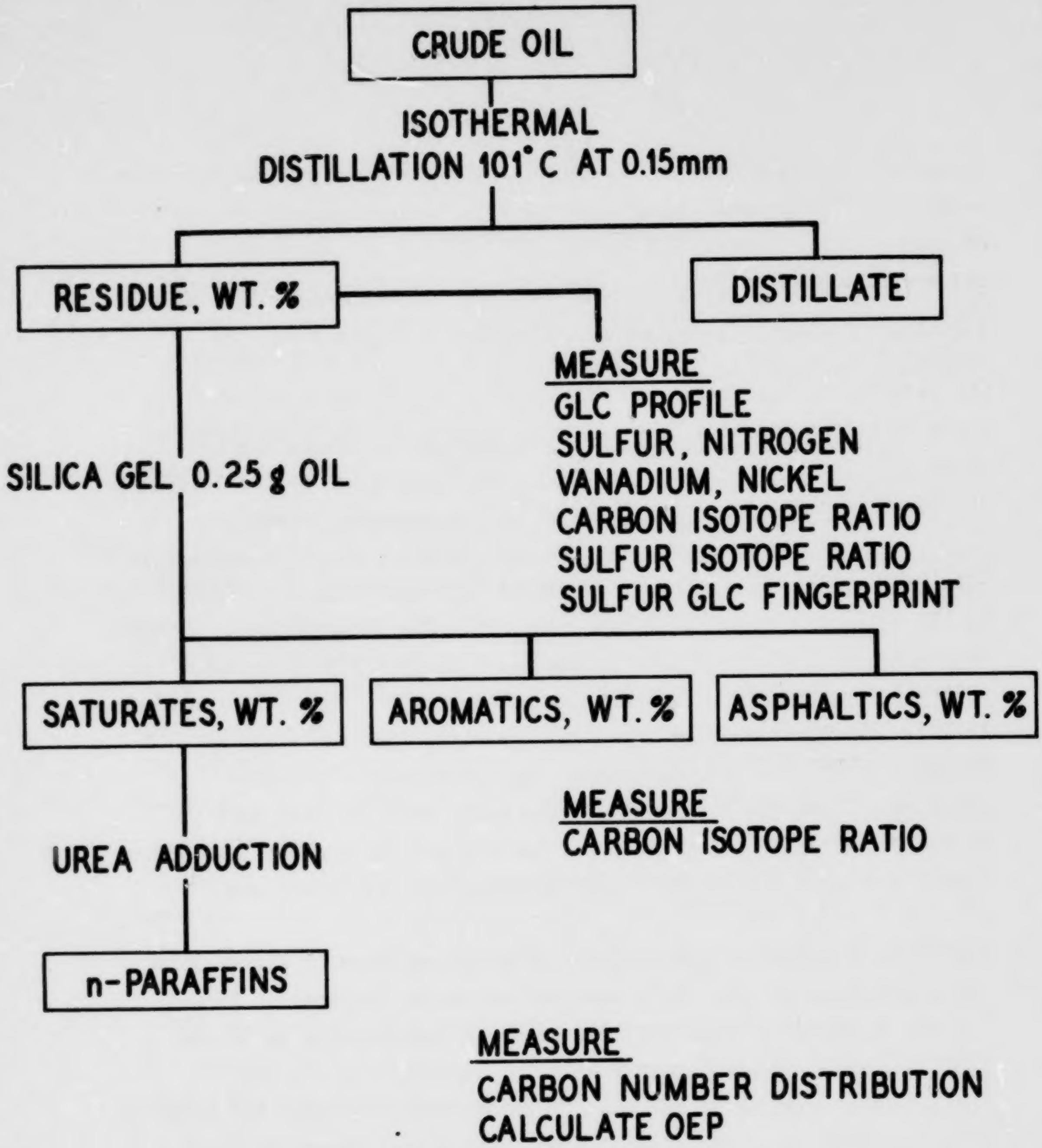

CRUDE OIL
ISOTHERMAL
DISTILLATION 101°C AT 0.15mm
RESIDUE, WT. %
DISTILLATE
MEASURE
GLC PROFILE
SULFUR, NITROGEN
VANADIUM, NICKEL
CARBON ISOTOPE RATIO
SULFUR ISOTOPE RATIO
SULFUR GLC FINGERPRINT
SILICA GEL 0.25 g OIL
SATURATES, WT. %
AROMATICS, WT. %
ASPHALTICS, WT. %
MEASURE
CARBON ISOTOPE RATIO
UREA ADDUCTION
n-PARAFFINS
MEASURE
CARBON NUMBER DISTRIBUTION
CALCULATE OEP

FIGURE 2 - SCHEMATIC DIAGRAM OF OIL POLLUTION SOURCE IDENTIFICATION SYSTEM

The amount of 600^{+}F bottoms recovered from the atmospheric equilibrated crude oils (stock tank liquids) varies from 30 to 99 weight per cent of the original charge. The values obtained for each individual crude oil are tabulated in Table 4. These values represent approximately the per cent of a crude oil spill that will persist after it has weathered a few days. Evaporation of the light ends will represent the majority of the loss. The magnitude of the clean-up operation in terms of volume can also be estimated. Except for the comparison of crude oils for their economic value this parameter serves little value for identification of a weathered unknown.

The initial portion of this study had as its objective the demonstration of the identification feasibility based on the carbon isotopic composition plus the five parameters of sulfur, nitrogen, vanadium, and nickel contents and the hydrocarbon gas chromatographic (GLC) profile. The values obtained for these six parameters plus the values of the sulfur isotopic composition on the eighty 600^{+}F bottoms are presented in Table 4. The diagnostic significance of these parameters is disclosed by an examination of the variation in each parameter. The variations observed for the four elemental parameters as well as the repeatability for each measurement are presented in Table 5. Conclusions regarding parameter values are based on repeatability.

The sulfur values fall into three ranges that allow each of the 600^{+}F bottoms to be classified as high, medium or low in sulfur. High sulfur bottoms are characteristic of crude oils from California, Mississippi, Florida, Venezuela, and the Middle East, and low sulfur bottoms of crude oils from Alaska, Louisiana, the North Sea and Nigeria. Exceptions to these generalizations have been observed.

TABLE 4

VALUES OF IDENTIFICATION PARAMETERS ON CRUDE OIL BOTTOMS

CRUDE OIL NO.	BOTTOMS WT. %	SULFUR	NITROGEN	VANADIUM	NICKEL	DEL C13	DEL S34 SULFUR ISOTOPE	GLC PROFILE
1	56.5	0.07	0.16	0.5	0.5	-30.2		5
2	56.7	0.11	0.22	0.6	2.1	-30.2		5
3	45.0	<0.05	0.11	<0.2	1.3	-29.5		3
4	45.7	<0.05	0.11	<0.1	2.0	-24.9		4
5	72.9	1.30	0.26	18.8	12.3	-29.3	-3.1	6
6	66.6	0.98	0.21	23.7	15.2	-30.4	-5.4	9
7	29.7	0.07	0.23	0.4	4.6	-22.4		2
8	85.2	1.70	0.53	49.1	72.0	-22.6	6.6	2
9	88.3	6.00	0.73	255.0	123.0	-22.8	17.6	B
10	59.1	2.90	0.18	11.2	7.5	-28.7	-4.3	1
11	49.2	0.26	0.08	1.1	0.8	-26.9	-1.8	B
12	61.6	0.11	0.06	<0.1	1.9	-26.8		4
13	70.6	0.29	0.13	1.0	2.3	-26.6		5
14	33.0	<0.05	0.02	<0.1	<0.1	-27.5	-7.9	3
15	82.6	4.91	0.11	15.6	14.1	-25.3	-7.1	2
16	76.9	3.91	0.22	14.4	15.7	-25.5	-8.2	1
17	53.4	1.65	0.06	<0.1	2.0	-24.9	-9.4	3
18	84.8	4.08	0.13	19.3	14.1	-25.1	-6.0	2
19	63.6	2.97	0.10	12.4	7.1	-25.0	-9.6	2
20	73.4	2.01	0.31	72.3	26.3	-26.5	0.3	5
21	58.6	<0.05	0.06	<0.2	0.1	-27.9		0
22	54.8	0.15	0.05	0.5	0.1	-28.1		0
23	60.0	0.45	0.09	0.5	0.1	-28.5		0
24	48.7	0.19	0.07	<0.2	0.1	-29.3		1
25	38.0	0.12	0.08	<0.2	2.7	-27.8		2
26	76.0	2.10	0.34	112.0	42.9	-26.3	2.3	1
27	72.0	3.80	0.20	73.3	23.8	-27.2	-8.7	0
28	63.0	2.34	0.07	4.7	9.5	-25.9	-5.8	1
29	63.7	2.39	0.09	10.0	2.8	-26.6		1
30	69.7	3.90	0.23	83.3	24.8	-26.6	-5.4	5
31	81.2	3.77	0.13	47.9	15.0	-26.7	-9.6	0
32	43.8	0.48	0.17	1.0	9.1	-27.2	2.3	0
33	59.4	0.54	0.25	5.6	24.5	-27.8	0.0	4
34	67.9	1.10	0.32	10.0	47.0	-28.3	1.3	4

TABLE 4 (CONTD.)

CRUDE OIL NO.	BOTTOMS WT. %	SULFUR	NITROGEN	VANADIUM	NICKEL	DEL C13	DEL S34 SULFUR ISOTOPE	GLC PROFILE
35	48.2	0.11	0.12	0.3	1.3	-27.6		9
36	49.6	0.10	0.02	0.6	5.6	-27.3		9
37	52.8	0.14	0.08	0.4	0.5	-28.3		2
41	70.1	1.40	0.12	18.9	10.2	-25.1	-11.2	9
42	45.2	0.05	0.08	<0.2	0.2	-23.9		9
43	67.7	1.37	0.21	57.1	31.5	-25.5	2.5	6
44	60.3	1.70	0.17	85.5	10.7	-26.3	6.6	4
45	98.2	4.40	0.50	466.0	103.0	-26.9	8.3	B
46	79.7	1.21	0.23	39.0	9.0	-27.1	8.7	B
47	51.6	0.18	0.16	0.5	1.1	-28.4		7
50	49.1	0.17	0.08	0.4	0.4	-28.3		9
51	71.7	5.18	0.14	92.0	25.2	-25.8	-13.2	1
52	76.7	4.39	0.24	82.9	39.8	-26.2	-14.3	3
53	76.6	4.65	0.20	52.4	60.2	-26.8	-14.2	2
54	78.7	4.83	0.24	58.9	66.9	-26.7	-14.4	1
55	72.8	4.07	0.16	43.2	38.5	-26.6	-13.5	3
56	60.8	0.16	0.16	0.8	3.1	-27.5		-
57	47.5	0.62	0.10	3.5	7.1	-27.4	5.0	9
58	73.0	0.89	0.16	11.0	88.2	-26.6	3.5	3
59	54.5	1.33	0.07	<0.3	0.8	-26.0	-4.6	7
60	54.1	1.37	0.05	0.4	1.2	-26.2	-3.7	6
61	81.3	0.12	0.14	0.9	14.3	-25.3		9
62	70.1	2.30	0.18	0.8	15.0	-27.4	13.9	1
63	73.3	2.13	0.18	0.7	14.7	-27.6	14.6	9
64	65.9	3.03	0.19	49.0	12.2	-26.9	-10.0	2
65	62.0	2.86	0.12	23.9	8.5	-26.6	-14.9	4
66	53.9	2.11	0.09	14.0	3.8	-26.3	-8.3	6
67	68.2	2.95	0.14	25.6	7.0	-26.6	-2.7	1
68	70.7	3.62	0.13	12.6	1.9	-26.1	-4.7	6
69	76.1	3.82	0.18	63.4	23.2	-26.9	-9.6	0
70	89.3	0.16	0.36	3.3	2.1	-29.5		5
71	63.9	1.25	0.28	76.3	27.9	-27.1	5.9	9
72	62.0	1.20	0.20	10.4	10.8	-25.3		4
73	99.2	1.84	0.12	9.4	4.6	-27.1		B

TABLE 4 (CONTD.)

CRUDE OIL NO.	BOTTOMS WT. %	SULFUR	NITROGEN	VANADIUM	NICKEL	DEL C13	DEL S34 SULFUR ISOTOPE	GLC PROFILE
74	87.2	3.52	0.24	15.1	17.4	-25.9	-4.0	B
75	78.2	5.69	0.67	246.0	100.0	-22.5	14.4	0
76	80.6	5.59	0.73	265.0	128.0	-22.4	17.8	B
77	38.8	0.17	0.02	<0.3	0.4	-25.6	-4.1	5
78	79.2	0.48	0.13	2.4	5.9	-27.1	-9.7	6
79	64.9	0.25	0.11	0.7	0.5	-26.7	-9.7	7
80	62.4	0.89	0.08	3.4	3.0	-26.6	-6.0	4
81	57.6	0.14	0.13	<0.3	1.1	-26.5	0.0	0
82	43.7	0.06	0.05	0.4	0.3	-29.1	-	2
83	94.5	2.40	0.48	232.0	70.0	-27.0	7.6	B
84	78.4	1.20	0.28	73.0	29.3	-25.8	-1.6	6

TABLE 5

RANGE OF VALUES FOR SULFUR, NITROGEN, VANADIUM AND NICKEL CONTENTS OF 600°F RESIDUES

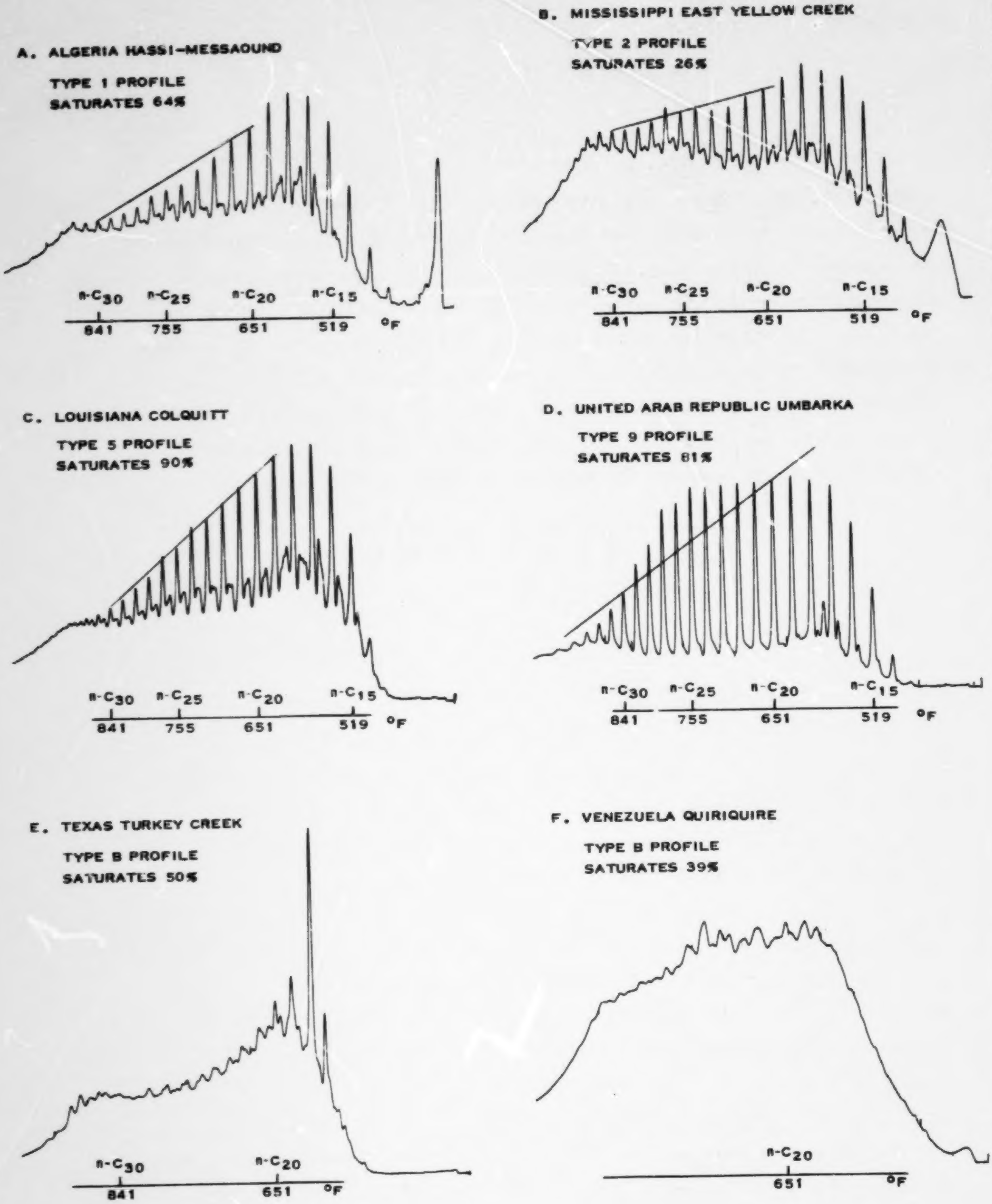
	VALUE	NO. OF CRUDE OILS	REPEATABILITY
SULFUR, WT. %			
HIGH	2-6	31	0.16 TO 0.24
MEDIUM	1-2	15	0.10
LOW	0.05-1	34	0.05 TO 0.07
NITROGEN, WT. %	.24-.73	14	0.06
	.15-.24	25	
	.03-.15	40	
VANADIUM, WPPM	112-466	6	
	24-92	21	5 @ 68 WPPM
	2-19	21	2 @ 14 WPPM
	<1	32	0.3 @ .3-2 WPPM
NICKEL, WPPM	60-128	9	
	20-47	14	
	2-17	38	2 @ 2-19 WPPM
	<1	19	

Nitrogen content, which covers a smaller range of values than sulfur content, serves to distinguish the few typically high nitrogen sources from the remainder. The California, South American and some Middle East bottoms have the highest nitrogen content. In general, the higher nitrogen contents are found in crude oil bottoms containing the higher vanadium and nickel contents.

The trace metals, vanadium and nickel, vary in amounts among the crude oils of the world.[16,17] Their presence at high levels deactivates catalysts for hydrodesulfurization, an important refining operation. These two trace metals and the ratio of their concentrations have been suggested by others for pollution source identification.[4,6,11,18] Our data support these suggestions. However, we agree with Kreider[4] that ratios are useful only if absolute values for individual elements are also reported. The range of contents for these two elements are sufficient to be significant identification parameters.

Hydrocarbon GLC Profile

On the basis of the variation in the hydrocarbon GLC profile among the eighty crude oils conclusions concerning the boiling range of the bottoms, the presence or absence of n-paraffins, and the presence of characteristic components can be made. Each profile consists of a number of peaks, which represent the n-paraffins, standing out above a broad envelope of incompletely separated components. Typical profiles are illustrated in Figure 3. The ability to distinguish between bottoms samples that exhibit profiles as different as 3A and 3F is obvious. In order to numerically classify the profiles for easy comparison a system based on the relative n-paraffin peak heights between n-C_{20} and n-C_{30} was developed. A number is obtained by connecting the peaks of these two n-paraffin components by a straight line and counting the number of peaks from C_{21} through C_{29} inclusive that touch or extend above the line. Each profile is assigned this number for facile recognition. For example, in Figure 3A through 3D the profile type is assigned on this basis. The location of the n-paraffin peaks and their corresponding atmospheric boiling points are given on the abscissa. If either or both of the two reference peaks do not appear, the profile is classified as broad and is assigned the letter B. The n-paraffins are either absent or too small to recognize in the latter cases (see Figure 3E and 3F). The frequency distribution of classification type among the sources is shown in Figure 4.



A. ALGERIA HASSI-MESSAOUND

TYPE 1 PROFILE
SATURATES 64%

B. MISSISSIPPI EAST YELLOW CREEK

TYPE 2 PROFILE
SATURATES 26%

C. LOUISIANA COLQUITT

TYPE 5 PROFILE
SATURATES 90%

D. UNITED ARAB REPUBLIC UMBARKA

TYPE 9 PROFILE
SATURATES 81%

E. TEXAS TURKEY CREEK

TYPE B PROFILE
SATURATES 50%

F. VENEZUELA QUIRIQUIRE

TYPE B PROFILE
SATURATES 39%

FIGURE 3 - TYPICAL GAS CHROMATOGRAPHIC PROFILES OF 600$^+$F RESIDUES

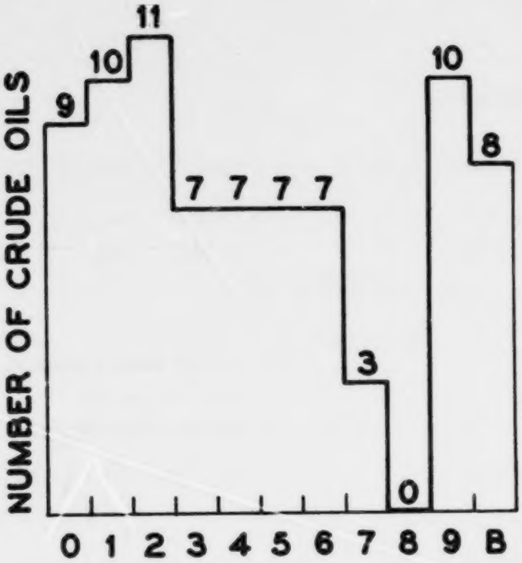


FIGURE 4 - FREQUENCY DISTRIBUTION OF HYDROCARBON GLC PROFILES BY CLASSIFICATION TYPE

The classification type is repeatable within ± one type for individual bottoms. The profile serves as an initial screening parameter to eliminate some potential pollution sources before proceeding to measure the other identification parameters.

The magnitude of peaks between those for n-paraffins C_{16} to C_{19} are noted to vary appreciably in height with crude oil source and can be useful to distinguish between similar profile types. Occasionally these peaks are larger than the n-paraffin peaks, for example, oil number 58 from Gabon. The other crude oil from Gabon, No. 57, also gave two large non-n-paraffin peaks between n-C_{17} and n-C_{18} and between n-C_{18} and n-C_{19}. The offshore Louisiana Ship Shoal crude oil, No. 81, exhibited similar behavior, which has been observed by others.[4]

Carbon Isotopic Composition

The carbon isotopic composition is expressed by the following equation:

$$\delta^{13}C_{PDB} = \left[\frac{^{13}C/^{12}C_{\ sample}}{^{13}C/^{12}C_{\ standard}} - 1 \right] 10^3 \qquad (5)$$

where $\delta^{13}C_{PDB}$ is the parts per thousand difference expressed in units of per mil, $^o/_{oo}$, between the $^{13}C/^{12}C$ ratio for the sample and that of an arbitrary standard. All data in this study are referred to the "PDB" standard, a carbonate fossil Belemnitella Americana of the Upper Cretaceous Peedee Formation of South Carolina.[12] The nominal natural abundance of these two stable isotopes is carbon-13, 1.1 per cent, and carbon-12, 98.9 per cent. The variations in the carbon isotopic composition occur as a consequence of environmental differences during the genesis of petroleum. The carbon isotopic composition is a valuable identification parameter because it undergoes little post-genesis alteration and, therefore, is characteristic for each crude oil. This fact also limits to a degree the usefulness of this parameter.

Erdman and Morris[6] demonstrated that crude oils from eighteen reservoirs in four Mississippi fields have the same carbon isotopic composition with a mean deviation of 0.1 per mil. This suggests a common source. This fact and the variation in the elemental composition among the five Mississippi crude oils, Nos. 15-19, Table 4, demonstrates the postulate of a common genesis source with subsequent migration into the present reservoirs where the oils underwent varying degrees of post-migration change.[6] The elemental compositions and the silica gel fraction percentages are the only differentiating parameters for these five crude oils. Identification of an unknown as being one from among these five crude oil sources provides a rigorous test of any matching scheme.

The carbon isotopic compositions of the 600$^+$F bottoms that comprise our crude oil sources range from -22 to -30 per mil (Table 4). The frequency distribution of this isotope ratio among the bottoms (Figure 5) indicates that 70% of the values fall within the 3 per mil range from 25.0 to 27.9. This distribution and range is similar to that found by Eckelmann[19] for 128 crude oils Devonian and younger. The carbon isotopic composition by itself is not normally sufficient to provide unique identification, but when applied in combination with the four elemental composition parameters, it is a diagnostic parameter that allows two otherwise equivalent crude oil sources to be distinguished.

The maximum observed differences in carbon isotopic ratios is between crude oils from Alaska, numbers 1, 2, 3, 5 and 6 and those from Southern California, numbers 7, 8, 9, 75 and 76. The Alaskan crude oils are isotopically light, i.e., most negative $\delta^{13}C$ values, compared to the California crude oils, which have the least negative $\delta^{13}C$ values. The Alaskan values vary from -30.4 to -29.3 per mil and the California values from -22.4 to -22.8 per mil. For these sources the carbon isotopic ratio alone is sufficient to distinguish these two sources; this is fortunate for pollution control in the North Pacific Ocean. The Alaskan sources are distinguished from one another by the significant difference in the sulfur and trace metal contents, i.e., the Cook Inlet crude oils have values an order of magnitude or more lower than the North Slope sources. Further applications of this parameter are discussed in Section IX.

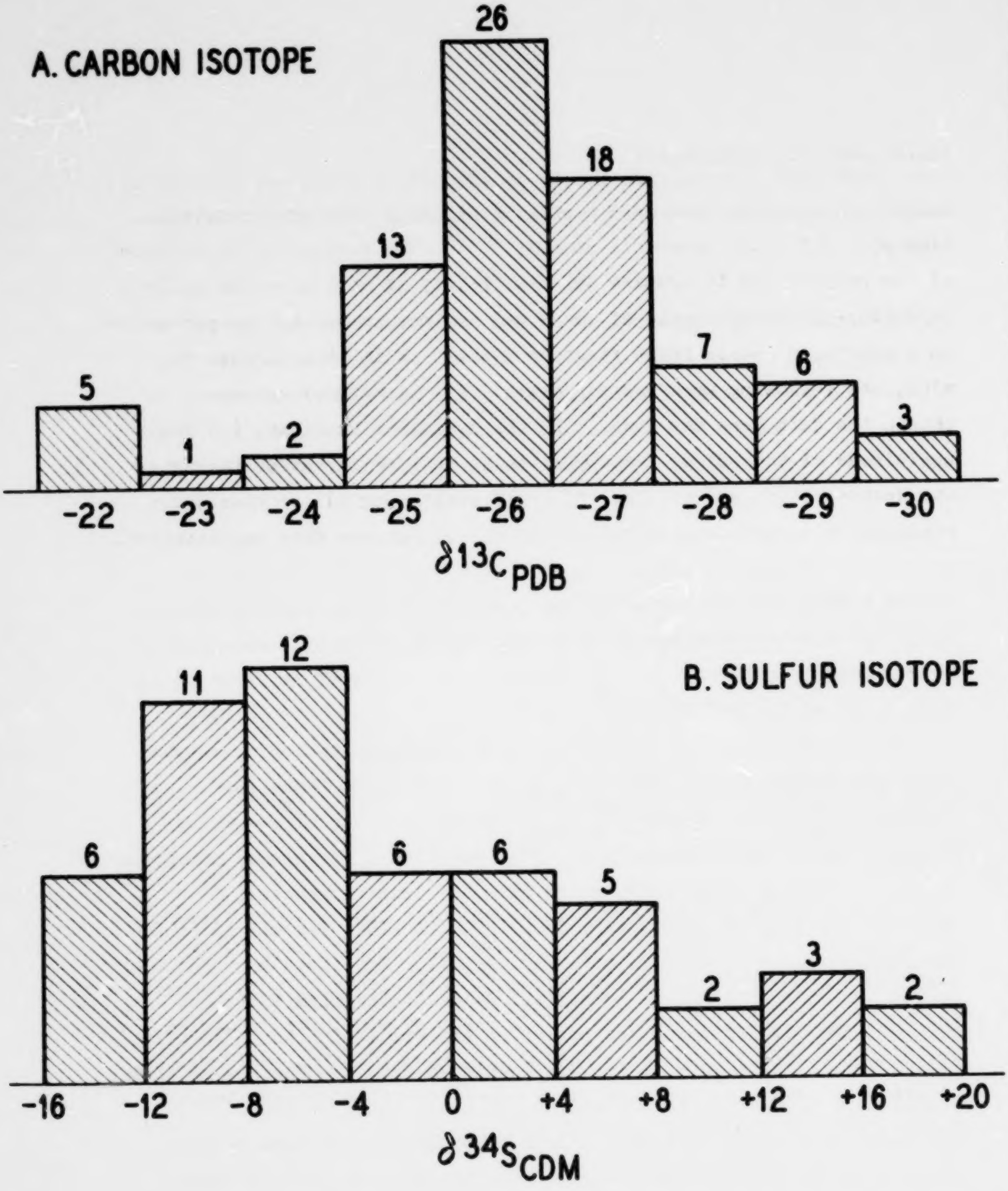


FIGURE 5 - DISTRIBUTION OF CARBON AND SULFUR ISOTOPIC COMPOSITIONS

Sulfur Isotopic Composition

Sulfur in petroleum possesses a wide variation in isotopic composition with different crude oil sources.[20,21] The purpose of this phase of the project was to examine the feasibility of utilizing the sulfur-34/sulfur-32 isotope ratio of crude oil bottoms as one of the parameters in a pollution source identification system. With this purpose in mind, the following work was performed: (1) techniques necessary to obtain the data were developed, (2) the data were obtained, (3) the usefulness of the sulfur isotope ratio as an identification parameter was demonstrated, and (4) the effect of weathering oil samples under simulated oil spill conditions on the sulfur isotope data was examined.

In the measurement of sulfur isotopic ratios, a comparison is made of the $^{34}S/^{32}S$ ratio of a sample with the $^{34}S/^{32}S$ ratio of a standard of known isotopic composition. The results are expressed in terms of the $\delta^{34}S$ value as defined below:

$$\delta^{34}S \ ^{o}/_{oo} = \left[\frac{(^{34}S/^{32}S)_{\text{sample}}}{(^{34}S/^{32}S)_{\text{standard}}} - 1 \right] \times 10^{3} \qquad (6)$$

$\delta^{34}S$ is a dimensionless quantity and is usually described in terms of a "per mil" or "del" value. The standard used as reference is the troilite phase from the Canon Diablo meterorite ($\delta^{34}S_{CDM} \equiv 0$) containing about 4.3% ^{34}S or having a $^{34}S/^{32}S$ ratio of 0.0450045. Samples containing more ^{34}S than the standard will have positive "del" values. In practice, most laboratories use a laboratory standard of known composition and then calculate the $\delta^{34}S_{CDM}$ value.

The sulfur isotopic ratios of 52 crude oil bottoms measured using the reductive hydrogenation approach are presented in Tables 4 and 6. With present techniques these measurements are limited to bottoms containing greater than 0.25 weight per cent sulfur. The $\delta^{34}S$ values range from +19.0 to -15.0 per mil and the distribution of values is shown in Figure 5B (Page 42). The spread and relatively even distribution of $\delta^{34}S$ values make the sulfur isotopic ratios an useful identification parameter.

The geographic distribution of the crude oils and their tentative sulfur isotopic composition are shown in Figure 6. The value of this parameter for the identification of an oil pollution source is illustrated by the following observations: A pollutant in the North Pacific Ocean off the Alaskan-Canadian coast could be distinguished as being from the North Slope fields (Alaska) or California based on $\delta^{34}S$ values of -3 to -5.4 and +6.6 to +17.8 per mil, respectively; and oils from offshore Louisiana (numbers 78, 79, 80), Venezuela (numbers 44, 45, 46), and Florida (numbers 51-55) could be distinguished based on $\delta^{34}S$ values of -6 to -10, +6.6 to +8.3, and -13.2 to -14.4 per mil, respectively. A similar situation exists in the Middle East in that the Israeli crude oils (numbers 62, 63) are isotopically much heavier than all other area sources measured; this difference ranges from 11.6 to 29.5 per mil. The majority of crude oils around the Persian Gulf are isotopically lighter than the standard, i.e., $\delta^{34}S$ values negative.

These observations are in marked contrast to the results predicted by a previous study.[2] However, another study concluded that sulfur isotopic ratios could be very valuable as an evidence point in identifying pollution sources.[18]

TABLE 6

SULFUR ISOTOPE COMPOSITION OF 600$^+$F BOTTOMS

BY THE PROPOSED REDUCTIVE (HYDROGENATION) PROCEDURE

EPA Crude Oil Number	Measured $\delta^{34}S$, o/oo	Average $\delta^{34}S$, o/oo	Source Description
5	- 3.4,-2.8	- 3.1	Prudhoe Bay, Alaska
6	- 5.9,-4.9,-5.5	- 5.4	W. Kaparuk, Alaska
8	7.2,5.9	6.6	Wilmington, California
9	19.1,15.5,18.1	17.6	Gato Ridge, California
10	- 4.3	- 4.3	Wasson, Texas
11	- 2.2,-1.3	- 1.8	Turkey Creek, Texas
15	- 7.1,-7.9	- 7.5	E. Yellow Creek, Mississippi
16	- 8.8,-9.8,-5.9	- 8.2	W. Yellow Creek, Mississippi
17	-10.3,-8.5	- 9.4	Nancy-Placid, Mississippi
18	- 6.1,-5.9	- 6.0	Pool Creek, Mississippi
19	- 9.6	- 9.6	West Heidelberg, Mississippi
20	0.3	0.3	Abu Arab A, Abu Dhabi
26	2.9,1.7	2.3	Gach Saran, Iran
27	- 8.7	- 8.7	Khafji, Kuwait (Neutral Zone)
28	- 5.8	- 5.8	Offshore Iran
30	- 4.4,-7.3,-4.6	- 5.4	Offshore Iran
31	-10.0,-10.0,-8.8	- 9.6	Wafra, Kuwait (Neutral Zone)
32	2.2,2.3	2.3	Hofra, Libya
33	0.0	0.0	Khuff, Libya
34	1.3	1.3	Amescas Beide, Libya
41	-11.2	-11.2	Alamein, United Arab Republic
43	2.5	2.5	Ghroud, United Arab Republic
44	6.8,6.8,6.2	6.6	Block 17, Maracaibo, Venezuela
45	9.4,7.1	8.3	Monagas, Venezuela
46	8.8,8.9,8.3	8.7	Quiriquire, Venezuela
51	-13.2	-13.2	Lake Trafford, Florida
52	-14.6,-14.0	-14.3	Sunniland, Florida
53	-13.3,-15.0	-14.2	Felda, Florida
54	-14.4	-14.4	Leheigh, Florida
55	-12.7,-14.2	-13.5	West Felda, Florida

TABLE 6 (Cont'd.)

SULFUR ISOTOPE COMPOSITION OF 600$^+$F BOTTOMS

BY THE PROPOSED REDUCTIVE (HYDROGENATION) PROCEDURE

EPA Crude Oil Number	Measured $\delta^{34}S$, °/oo	Average $\delta^{34}S$, °/oo	Source Description
57	5.0	5.0	Batanga, Gabon
58	2.6,4.3	3.5	Tehenque, Gabon
59	- 4.6	- 4.6	Bu Hasa I, Abu Dhabi
60	- 3.7	- 3.7	Murban-Bab-Bu-Hasa, Abu Dhabi
62	13.4,14.4	13.9	Heletz, Israel
63	14.6	14.6	Kokhav, Israel
64	-10.0	-10.0	Magwa-Ahmadi, Kuwait
65	-15.7,-14.0	-14.9	Offshore, Qatar
66	- 8.3	- 8.3	Offshore, Qatar
67	- 2.5,-2.6,-3.0	- 2.7	Ghawar, Saudi Arabia
68	- 4.1,-5.3	- 4.7	Qatif, Saudi Arabia
69	- 9.9,-8.7,-10.1	- 9.6	Safaniya, Saudi Arabia
71	5.9	5.9	Payoa, Colombia
74	- 3.9,-4.0	- 4.0	Santa Marie del Mar, Cuba
75	14.4	14.4	Lompac, California
76	17.8	17.8	St. Maria Valley, California
77	- 4.4,-3.8	- 4.1	Colquitt, Louisiana
78	- 9.7,-9.1,-10.2	- 9.7	Delta West, Louisiana (Offshore)
79	- 9.7	- 9.7	Delta West, Louisiana (Offshore)
80	- 6.0	- 6.0	Eugene Island, Louisiana (Offshore)
83	7.6	7.6	Monagas, Venezuela
84	- 1.6	- 1.6	Ecuador

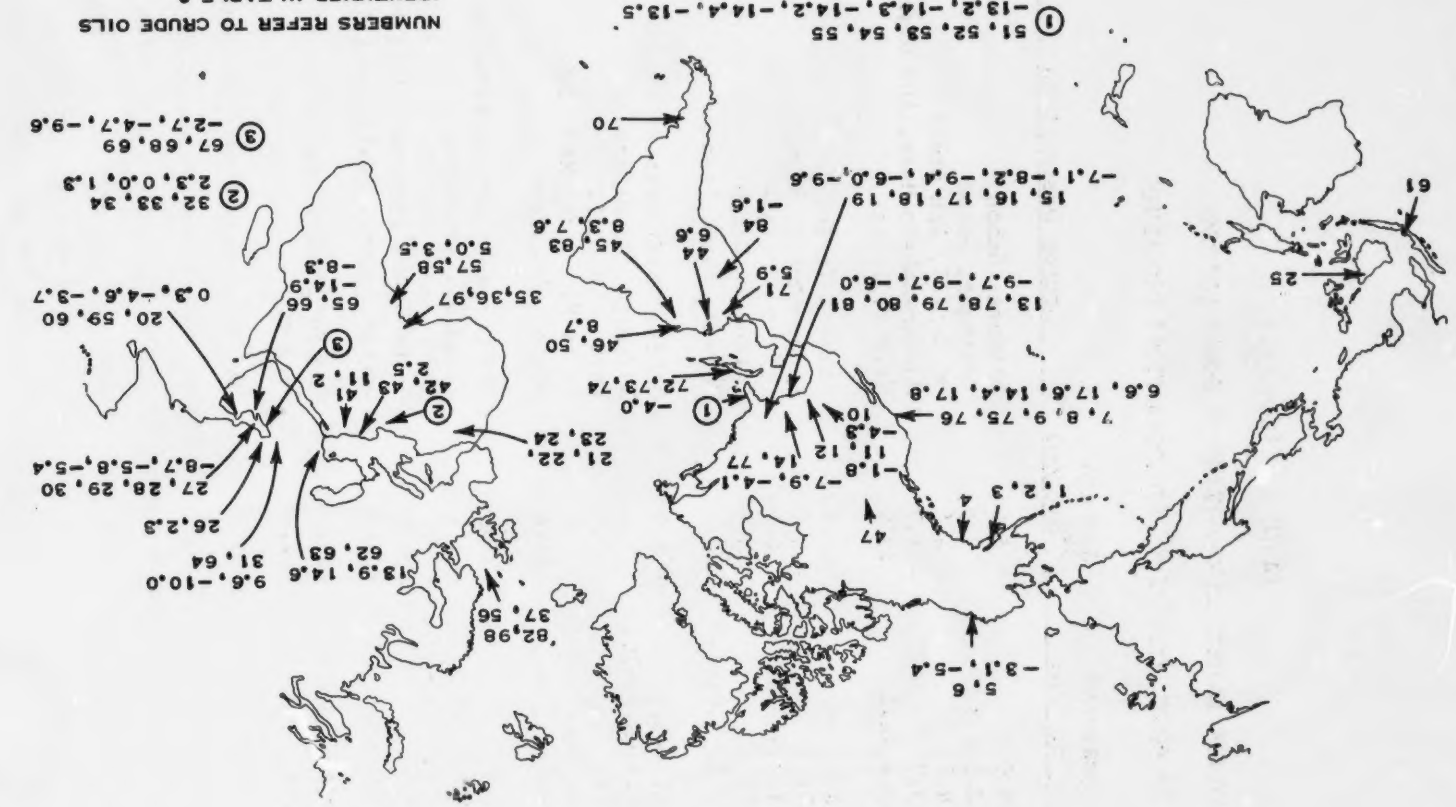

5, 6
-3.1, -5.4
1, 2, 3
4
47
-1.8
11, 12
-4.3
10
-7.9, -4.1
14, 77
7, 8, 9, 75, 76
6.6, 17.6, 14.4, 17.8
13, 78, 79, 80, 81
-9.7, -9.7, -6.0
15, 16, 17, 18, 19
-7.1, -8.2, -9.4, -6.0, -9.6
①
-4.0
72, 73, 74
71
5.9
84
-1.6
44
6.6
46, 50
8.7
45, 83
8.3, 7.6
70
61
25
21, 22,
23, 24
'82, 98
37, 56
②
42, 43
2.5
41
11, 2
13.9, 14.6
62, 63
9.6, -10.0
31, 64
26, 2.3
27, 28, 29, 30
-8.7, -5.8, -5.4
③
20, 59, 60
0.3, -4.6, -3.7
65, 66
-14.9
-8.3
35, 36, 97
57, 58
5.0, 3.5
① 51, 52, 53, 54, 55
-13.2, -14.3, -14.2, -14.4, -13.5
② 32, 33, 34
2.3, 0.0, 1.3
③ 67, 68, 69
-2.7, -4.7, -9.6
NUMBERS REFER TO CRUDE OILS
IDENTIFIED IN TABLE 2.

FIGURE 6 - GEOGRAPHICAL DISTRIBUTION OF CRUDE OIL SOURCES AND SULFUR ISOTOPIC COMPOSITION

To be used as an identification parameter, the sulfur isotopic ratio should be independent of the other measured parameters. Plots of the $\delta^{34}S$ values against the $\delta^{13}C$ values, the sulfur and vanadium concentration were made and the $\delta^{34}S$ values appeared to be independent of these other parameters.

An analysis of the data obtained in cases where duplicate measurements were made indicates that in most cases the data has a precision of ±1 per mil which is sufficient for these exploratory studies. Using refined techniques it should be possible to improve the precision to ± 0.2 per mil since this precision has been attained in several instances. We have determined that in several cases where the precision hoped for was not attained, the SO_2 samples contained traces of impurities that probably interfered with the isotope ratio measurement. Experiments have indicated that a modification of the combustion technique results in improved purity of the SO_2 samples.

A direct comparison between the sulfur isotopic ratios obtained in this study and those measured in published studies is not possible because of the different oil sources and measurement techniques used in this study. Previous workers did not make their measurements on the 600^{+}F bottoms but it is expected that the sulfur isotopic ratio of the total crude would be very similar.[22] The general agreement of the data in Table 7 indicates that our results are equivalent to those found by others and supports both our choice of measurement procedures and the application of sulfur isotopes as an identification parameter. The sulfur isotopic ratios measured by other workers are summarized in Appendix M in order to provide a convenient, readily-accessible source of data for crude oils. These data can be used to evaluate the overall identification potential of this parameter for sources and circumstances outside the scope of this study.

TABLE 7

COMPARISON OF SULFUR ISOTOPIC COMPOSITION WITH LITERATURE VALUES

	This Work			Previous Work		
Oil Source	EPA No.	% S	$\delta^{34}S$	% S	$\delta^{34}S$	Ref
California, Wilmington	8	1.7	6.6	1.5	6.8	23
Venezuela, Lake Maracaibo	44	1.7	6.6		6.1	18
Venezuela, Lake Maracaibo	46	1.2	8.7			
Kuwait, Wafra	31	3.8	-9.6	3.9	-9.8	23
Saudi Arabia, Ghawar (Haradh)	67	3.0	-2.7	2.1	-1.9	23
Saudi Arabia, Safaniya	69	3.8	-9.6	3.0	-8.5	23

The application of $\delta^{34}S$ values to distinguish between pairs of crude oils in which the other identification parameters are similar is described for oil numbers 30 and 69 and for numbers 65 and 67 by the data in Table 8. There is a clear distinction between the oils only when the sulfur isotopic data are included.

TABLE 8

APPLICATION OF SULFUR ISOTOPIC COMPOSITION

EPA Crude Oil Number	30 vs	69	65 vs	67
Oil Source	Iran	Saudi Arabia	Qatar	Saudi Arabia
$\delta^{13}C_{PDB}$	-26.6	-26.6	-26.6	-26.6
Sulfur (Wt. %)	3.90	3.82	2.86	2.95
Nitrogen (Wt. %)	0.23	0.18	0.12	0.14
Vanadium (W ppm)	83.30	63.40	23.90	25.60
Nickel (W ppm)	24.80	23.20	8.44	6.97
Vanadium/Nickel Ratio	3.36	2.73	2.83	3.67
Sulfur/Nitrogen Ratio	16.96	21.22	23.83	21.07
$\delta^{34}S$ (Average)	- 5.4	- 9.6	-14.9	- 2.7

In experiments to determine what the effect of weathering is on the sulfur isotopic ratios, the $\delta^{34}S$ values were obtained from several of the weathered samples from oils 83 and 84. (Data presented in Section IX.) There was no trend observed in the $\delta^{34}S$ values versus length of time weathered and it is evident the $\delta^{34}S$ values did not change under the conditions of our weathering experiments.

The $\delta^{34}S$ values obtained for five oils using the oxidative route and the reductive route are compared in Table 9. The differences observed are outside the expected range of repeatability and in each case the value from the oxidative route is more positive. A systematic error is suspected in one of the techniques used. There is no a priori reason the results should not agree but the source of disagreement was not isolated.

TABLE 9

COMPARISON OF SULFUR ISOTOPE RATIOS BY THE

OXIDATIVE AND REDUCTIVE METHODS

Crude Oil Number	$\delta^{34}S$ (Oxidative)	$\delta^{34}S$ (Reductive)
9	22.4 ‰	17.6 ‰
15	- 5.7	- 7.1
17	- 5.1	- 9.4
68	- 2.0	- 4.7
74	- 2.2	- 4.0
*BKE Elemental Sulfur	-11.2	-

*The expected $\delta^{34}S$ value, regardless of method, is -11.8 ‰.

The measured values of these preceeding selected parameters on the 600^{+}F bottoms of crude oils from the major producing areas of the world cover a sufficient range and distribution to offer strong evidence for oil pollution source identification. The techniques to apply these variations to the identification problem are discussed in Section VIII.

Sulfur Gas Chromatographic Profile

Sulfur is the most abundant element other than carbon and hydrogen present in crude oils. The total sulfur content varies from less than 0.05 to greater than 6.0 weight per cent and is a useful identification parameter. This sulfur is present as a wide boiling range of organic sulfur compounds; up to 200 individual sulfur compounds have been identified by U.S. Bureau of Mines chemists.[24] These include thiols (mercaptans), sulfides, disulfides and thiophenes. The development of a sulfur-selective gas chromatographic detector led Adlard[5] to propose the measurement of a sulfur gas chromatographic (GLC) profile analogous to the hydrocarbon GLC profile as an aid to pollution source identification. The potential value of this profile was demonstrated in the initial publication. The variation in the sulfur GLC profile was investigated on our collection of crude oils with the objective to evaluate its general usefulness.

The sulfur-selective detector is based on flame emission photometry.[25] The radiant energy emitted at 394 nm when the gas chromatograph effluent is burned in a hydrogen flame arises predominantly from the sulfur atoms present. The background signal from hydrocarbons is relatively small. The response of this detector gave a reproducible and unique profile for each crude oil sample. Forty-eight representative 600^{+}F bottoms that contained more than 1% sulfur were examined.

This was the lowest level of total sulfur, for which a sulfur GLC profile could be obtained without distortion from the background noise on our equipment.

The sulfur GLC profiles ("fingerprints") are classified into six types, three of which are shown in Figure 7. Type A, which is distinguished by two broad partially resolved peaks of equal magnitude, is characteristic for 6 crude oil sources, Nos. 15, 16, 20, 30, 43 and 69. Type B, which consists of 8 different sources, Nos. 17, 28, 29, 46, 59, 60, 66 and 74, is characterized by a sharp rise to a large, broad partially-resolved center peak followed by a smaller broad peak. The Type C profile is found for 13 crude oil sources and contains several resolved peaks preceeding the Type B peaks. These 13 Type C profiles are for Nos. 10, 18, 19, 26, 27, 31, 41, 64, 65, 67, 68, 71 and 80. Eight of the 600^{+}F bottoms show only a broad background envelope with no distinctive peaks or highlights, Type D. The last two types consist of 5 profiles with a broad large peak and 8 profiles with a large broad peak with two sharp characteristic peaks. The latter 8 include 5 South Florida Basin crude oils and 3 California oils, which are low in saturates and high in sulfur.

As with the hydrocarbon GLC profile, this sulfur profile exhibits sufficient variety to serve as an initial screening parameter for high and medium level sulfur residues. The attractive feature of this parameter is the fact that the profile is unaffected by weathering, which apparently destroys n-paraffins by biological degradation.[5] This alteration by weathering reduces the usefulness of the hydrocarbon GLC profile as a screening parameter.

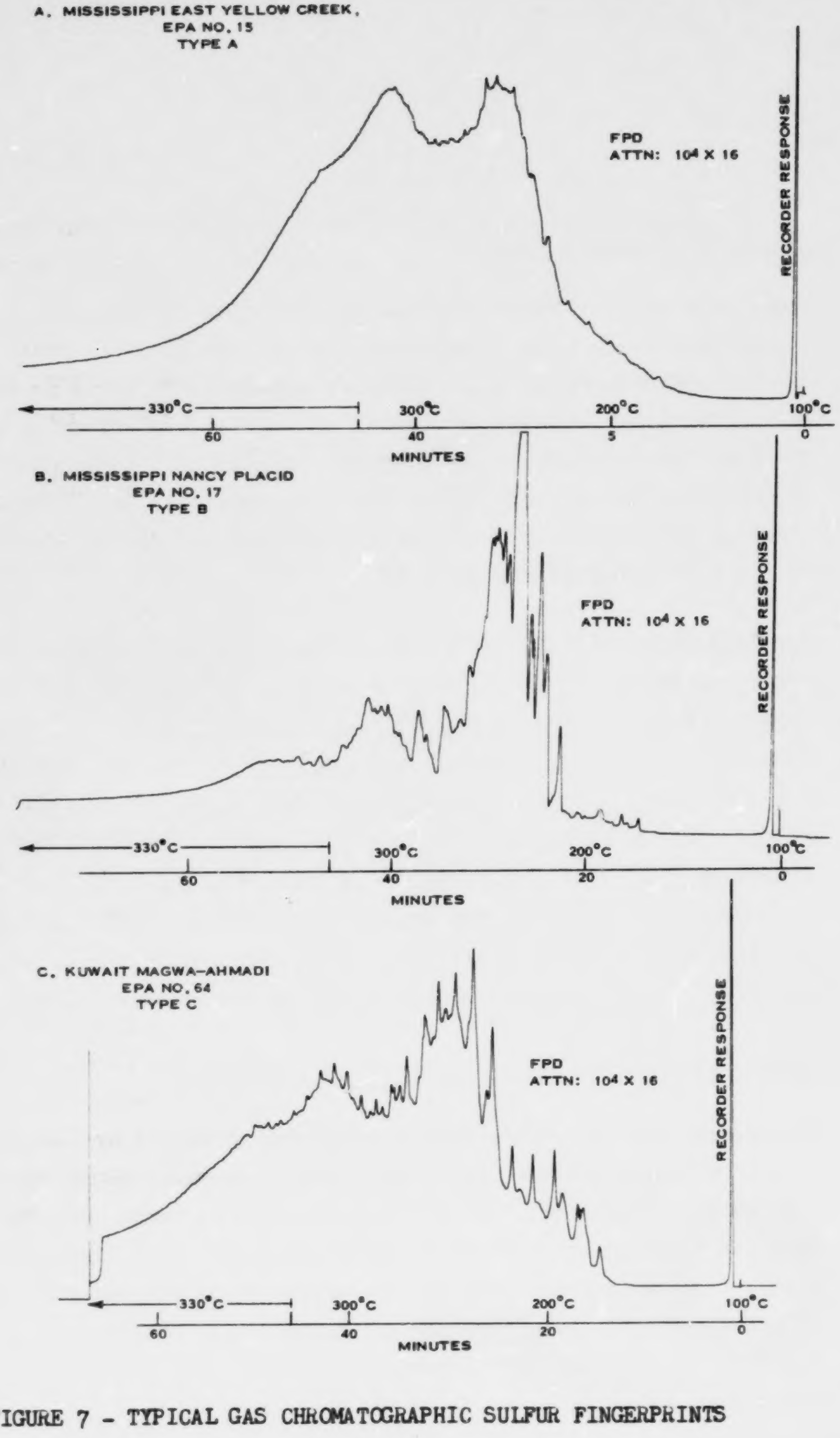


FIGURE 7 - TYPICAL GAS CHROMATOGRAPHIC SULFUR FINGERPRINTS

Silica Gel Fractionations

Where sufficient differences exist in the values for the previous parameters, unequivocal identifications are feasible. In other cases, the diagnostic power of these measured parameters fails to permit any definitive conclusions as to source. Further characterization of the 600$^+$F bottoms was made by fractionation of each into three portions: saturates, aromatics, and asphaltics. The amount in each portion was measured and additional measurements were then made on each fraction. The data is summarized in Table 10.

The distribution of the 600$^+$F bottoms among the three silica gel fractions (Table 10) varies from 19 to 83 weight per cent for the saturates, from 6 to 67 weight per cent for the aromatics, and from 0.3 to 31.4 weight per cent for the asphaltics. The per cent recovery varied from 73 to 102%. Although experience indicates that the recovery should exceed 85%, there will be sources which may contain polar compounds such as naphthenic and tar acids that are retained on the silica gel. High boiling waxes (saturates) are also retained and are recovered from heated columns. A low recovery indicates conclusions should be carefully drawn and the sample should be examined more fully.

Carbon Isotopic Composition of Silica Gel Fractions

The carbon isotopic composition was measured on each fraction from the silica gel separations. The carbon isotopic composition of the 600$^+$F bottoms is compared with that of each fraction in Table 10. The saturate fraction is normally equal to or isotopically lighter, i.e., a more negative number, than the bottoms by about one per mil. The aromatic and asphaltic fractions are isotopically heavier, i.e., less negative values, than the bottoms.

TABLE 10

VALUES FOR CARBON ISOTOPIC COMPOSITION ON CRUDE OIL BOTTOMS AND THEIR SILICA GEL FRACTIONS

CRUDE OIL NO.	TOTAL CRUDE DEL C-13	SATURATES		AROMATICS		ASPHALTICS	
		WT. %	DEL C-13	WT. %	DEL C-13	WT. %	DEL C-13
1	-30.2	57.0	-31.7	37.3	-29.3	5.7	-29.6
2	-30.2	57.3	-31.8	38.6	-30.5	4.1	-29.5
3	-29.5	67.3	-31.0	29.5	-29.3	3.1	-29.2
4	-24.9	67.2	-26.0	29.0	-24.7	3.8	-24.2
5	-29.3	40.9	-30.3	51.5	-29.2	7.6	-29.3
6	-30.4	50.1	-31.3	42.2	-30.6	7.7	-29.9
7	-22.4	60.0	-23.2	33.1	-22.8	6.9	-21.6
8	-22.6	27.9	-24.6	57.7	-23.4	14.4	-22.7
9	-22.8	13.2	-23.6	62.5	-22.5	24.3	-22.3
10	-28.7	40.3	-30.1	49.9	-29.1	9.8	-28.3
11	-26.9	50.3	-28.3	41.2	-26.9	8.5	-27.0
12	-26.8	67.7	-28.8	28.9	-27.3	3.4	-27.2
13	-26.6	54.2	-27.9	38.7	-27.3	7.0	-27.2
14	-27.5	93.1	-29.1	6.3	-	0.7	-
15	-25.3	26.2	-25.0	64.1	-25.1	9.7	-25.5
16	-25.5	36.8	-25.5	53.6	-25.1	9.6	-25.2
17	-24.9	62.2	-25.1	35.7	-24.2	2.1	-24.3
18	-25.1	32.7	-25.2	58.5	-25.1	8.8	-25.6
19	-25.0	52.7	-25.0	39.5	-25.0	7.8	-24.9
20	-26.5	39.3	-26.4	50.9	-25.1	9.3	-25.0
21	-27.9	77.2	-28.5	20.4	-27.8	2.4	-26.7
22	-28.1	81.0	-28.3	17.2	-27.6	1.9	-28.1
23	-28.5	54.6	-28.7	39.3	-27.9	6.1	-28.1
24	-29.3	64.4	-29.4	32.1	-28.5	3.6	-28.6
25	-27.8	61.9	-29.2	34.4	-27.9	3.7	-28.5
26	-26.3	39.4	-27.5	49.8	-26.8	10.8	-25.8
27	-27.2	33.0	-27.9	57.6	-26.9	9.5	-27.3
28	-25.9	52.5	-26.1	42.3	-25.6	5.1	-25.8
29	-26.6	48.3	-26.8	45.9	-26.2	5.7	-24.7
30	-26.6	36.7	-27.1	55.2	-26.8	8.1	-26.8
31	-26.7	38.7	-27.8	54.6	-27.2	6.7	-27.2
32	-27.2	62.2	-28.3	32.5	-27.1	5.3	-26.4
33	-27.8	60.8	-29.1	33.6	-27.6	5.6	-27.0
34	-28.3	51.0	-29.1	40.7	-27.6	8.3	-26.7

TABLE 10 (CONTD.)

CRUDE OIL NO.	TOTAL CRUDE DEL C-13	SATURATES		AROMATICS		ASPHALTICS	
		WT. %	DEL C-13	WT. %	DEL C-13	WT. %	DEL C-13
35	-27.6	67.2	-28.4	28.5	-26.5	4.3	-25.2
36	-27.3	63.5	-28.3	32.8	-26.8	3.7	-23.9
37	-28.3	76.7	-28.9	20.7	-28.5	2.6	-27.5
41	-25.1	50.3	-25.9	37.3	-24.6	12.4	-21.0
42	-23.9	81.0	-25.5	17.5	-23.7	1.5	-24.8
43	-25.5	42.6	-26.2	47.7	-25.1	9.7	-25.9
44	-26.3	53.3	-27.2	38.3	-26.0	8.4	-26.0
45	-26.9	15.7	-28.2	62.2	-27.9	22.1	-27.3
46	-27.1	38.6	-27.3	48.8	-27.7	12.7	-27.6
47	-28.4	68.5	-29.4	28.1	-28.8	3.5	-27.3
50	-28.3	76.1	-28.6	20.2	-27.2	3.7	-25.5
51	-25.8	25.4	-26.1	66.9	-26.4	7.7	-26.3
52	-26.2	24.9	-27.9	60.6	-26.9	14.5	-27.1
53	-26.8	26.4	-27.9	65.8	-27.3	7.8	-27.2
54	-26.7	27.3	-28.4	62.9	-27.3	9.8	-26.4
55	-26.6	30.5	-27.2	61.2	-27.1	8.3	-26.6
56	-27.5	61.9	-27.6	34.2	-27.2	3.9	-26.5
57	-27.4	64.1	-26.9	28.6	-26.7	7.3	-27.1
58	-26.6	51.3	-26.6	42.8	-26.1	5.8	-26.0
59	-26.0	59.9	-26.0	35.5	-25.9	4.6	-25.3
60	-26.2	60.6	-27.3	35.9	-25.7	3.4	-25.1
61	-25.3	67.8	-25.2	26.1	-24.7	6.1	-24.0
62	-27.4	36.7	-28.1	48.7	-27.3	14.5	-24.1
63	-27.6	45.3	-28.3	46.4	-27.3	8.4	-24.1
64	-26.9	39.5	-27.1	53.6	-26.8	6.8	-26.7
65	-26.6	43.2	-26.8	48.7	-26.1	8.1	-26.2
66	-26.3	48.5	-26.6	44.2	-25.9	7.2	-26.2
67	-26.6	42.9	-26.7	44.6	-26.1	12.5	-26.3
68	-26.1	35.4	-26.3	52.0	-26.3	12.6	-26.3
69	-26.9	32.4	-26.9	48.6	-26.7	19.1	-27.0
70	-29.5	45.6	-30.0	42.8	-28.9	11.6	-28.3
71	-27.1	54.6	-27.3	36.9	-26.8	8.5	-26.9
72	-25.3	43.9	-25.8	38.6	-24.6	17.5	-24.6
73	-27.1	46.2	-26.9	41.6	-26.9	12.2	-27.3

TABLE 10 (CONTD.)

CRUDE OIL NO.	TOTAL CRUDE DEL C-13	SATURATES		AROMATICS		ASPHALTICS	
		WT. %	DEL C-13	WT. %	DEL C-13	WT. %	DEL C-13
74	-25.9	21.2	-26.2	47.4	-25.5	31.4	-26.0
75	-22.5	14.6	-22.7	64.1	-22.4	21.3	-21.7
76	-22.4	14.5	-22.8	65.1	-22.1	20.5	-21.9
77	-25.6	89.5	-25.2	9.8	-24.0	0.7	-24.5
78	-27.1	55.7	-27.3	36.9	-26.3	7.4	-26.1
79	-26.7	61.3	-26.7	31.6	-26.1	7.1	-25.8
80	-26.6	62.1	-26.7	33.0	-26.1	5.0	-26.0
81	-26.5	80.2	-26.5	17.1	-25.9	2.6	-26.0
82	-29.1	78.5	-28.6	19.2	-28.1	2.4	-27.4
83	-27.0	30.3	-27.8	53.5	-27.1	16.2	-27.3
84	-25.8	35.2	-27.6	53.3	-25.9	11.5	-25.3

These observations are expected based on the hypothesis of hydrocarbon formation. The mechanism of light hydrocarbon formation by thermal cracking of organic material favors rupture of the $C^{12} - C^{12}$ bond over the $C^{12} - C^{13}$ bond (by about 8% in simple molecules). The remaining residual organic material will be isotopically heavier with respect to the original. This mechanism implies a dehydrogenation resulting in double bond formation in the parent molecules; as this process continues polyenes may form, which can aromatize or polymerize. This would lead to aromatics and asphaltene-type compounds, respectively, that are isotopically heavier than the non-aromatics (saturates). The validity of this hypothesis is confirmed in part by Silverman and Epstein[26] for aromatics and by Silverman for asphaltenes.[27]

Examination of the carbon isotope data on the silica gel fractions 600^{+}F bottoms show that the saturates are isotopically lighter than 600^{+}F bottoms ($\Delta = 0.6$ or greater) for 41 of 77 sources.

Normal Paraffins and Odd-Even Predominance Curves

The n-paraffins are isolated from the saturate fraction by urea adduction. When urea crystallizes from solution the n-paraffins are trapped within the crystal lattice, the dimensions of which accommodate selectively the linear molecules but exclude the branched and cyclic paraffin molecules. The relative n-paraffin distribution is obtained by normalization of the measured weight per cent n-paraffins from C_{13} through C_{38}. The n-paraffin distribution is utilized to calculate the odd-even predominance or OEP, which is a measure of deviation from an unbiased distribution of n-paraffins of odd and of even carbon numbers as a function of carbon number.[28] The OEP values are computed according to the following equation:

$$\mathrm{OEP}_{i+2} = \left[\frac{C_1 + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}}\right]^{(-1)^{i+1}} \qquad (7)$$

where C_i is the relative weight per cent of a n-paraffin containing i carbons per molecule. The computed OEP value is assigned to the n-paraffin containing i+2 carbon atoms in the molecule. The OEP value is unity for an unbiased distribution, greater than unity if odd-carbon numbered n-paraffins predominate and less than unity if even-carbon numbered n-paraffins predominate. The OEP values are plotted as a function of carbon number from C_{15} to C_{35}. The shape of the resulting curve, i.e., the location and number of maxima and minima, is characteristic of the crude oil genesis source and therefore, of the crude oil itself. The shape of the curve varies among unrelated crude oils and is similar for related samples. Typical OEP curves are illustrated in Figure 8. The curves in Figure 6A are for two crude oils from Nigeria, Nos. 35 and 36, and two from the Southern Alaskan coast, Nos. 3 and 4. Four offshore Louisiana, Nos. 78, 79, 80, and 81, and eight western shore Persian Gulf sources, Nos. 59, 60, 64, 65, 66, 67, 68, and 69 give similar curves in each case, Figure 6B and 6C. This suggests a common geologic origin for each group of crude oils. However, the similarity prevents application of this parameter to distinguish among the sources within each group. Distinctive OEP curves characterize related oils in other oil producing areas of the world and these curves are significantly different from those examples in Figure 8. On this basis the OEP curves could contribute to pollution source identification.

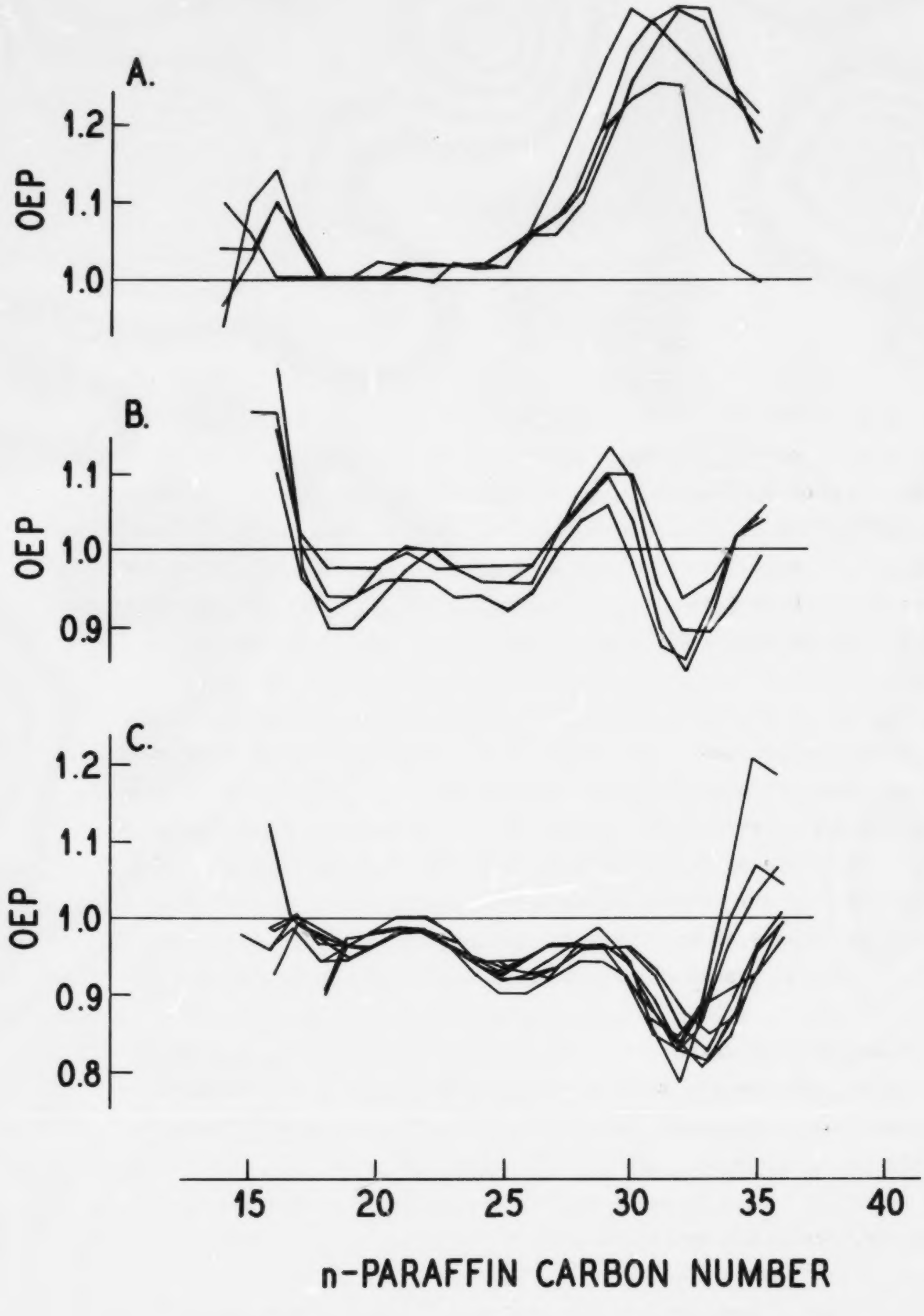


FIGURE 8 - TYPICAL ODD-EVEN PREDOMINANCE (OEP) CURVES

SECTION VIII

COMPARISON TECHNIQUES

The utilization of a multiparameter oil pollution source identification system requires the completion of three tasks: collection of pollutant samples and samples representative of potential sources, measurement of the identification parameters on each sample, and comparison of the values of the measured parameters of the pollutant sample with those of the potential source samples to identify the pollution source. The procedures for sample handling and parameter measurement have already been described. Methods used in the comparison of parameter values are described in this section.

The potential sources can be in the form of a data library, which consists of the measured values of the identification parameters for a large number of oils. Alternatively, the potential sources can be samples from several suspect sources in the vicinity of the spill at the time of the spill. In either case, the correct identification is possible only when the "real" source is among the suspect sources. The present lack of an officially sanctioned oil pollution source identification system makes establishment of a data library premature.

In cases where a small number of suspect source samples exists, it is possible to compare sample parameters without using a data handling system. In these cases, the bias of the individual analyst may influence the identification.

Two computer-based comparison systems were applied to the identification of an "unknown" as being equivalent to one of the sources in our data library. Computerized systems have the advantages that analyst bias is eliminated and that comparisons of a large number of oils are readily made. The first system is based on Qwick-Qwery (QQ)[29], a computer data handling system, which is applied to match, in sequence, each of the parameters for the unknown with those in the data library. Those sources that match on 7 of 7, 6 of 7, etc., of the parameters are printed out. A match of any one of the parameters is scored if the library data fall within an assigned ± value of the unknown. In order for an oil to be identified as the oil pollution source, the pollution sample and the potential source should match in all of the measured parameters.

The second computer-based comparison system is based on a statistical procedure that incorporates the fundamentals of multivariate normal analysis. A detailed description of the procedure is given in Appendix N. Using this procedure, each of the oils in the library is compared with the unknown and the "closeness" of match of the identification parameters is calculated in terms of the discriminant variate for each potential source. The computer output ranks the potential sources according to increasing value of the discriminant variate. The discriminant variate will be zero if the identification parameters for the unknown perfectly match those of a library source. The expected value of the discriminant variate for two oils from the same source but subject to measurement variations is equal to the number of parameters tested, i.e., a value of 6 is expected, if 6 parameters are applied to identification.

A decision problem arises using either of the computer-based comparison systems when less than a perfect match is attained between an unknown and a library oil. Using the Qwick-Qwery system when no or more than one perfect match occurs the data of each of the prime suspect sources is examined and a decision made on the basis of the data and the geographical location of the source. Although Qwick-Qwery reduces the number of suspects to the most likely sources, the final identification is still subject to individual bias.

Using the statistical comparison system a decision must be made as to what value of the discriminant variate eliminates an oil from consideration as the pollution source. An approximation to this decision can be achieved by estimation of the discriminant variate value when the number of separate samples from each potential source is equal to the number of identification parameters matched. If the unknown and a potential source are the same based on 6 parameters, the probability is 95% that the value of the discriminant variate will be 20 or less. With 5 parameters the 95% probability value of the discriminant variate increases to 40. These values were used in evaluation of this system to identify oils.

It is recommended that both Qwick-Qwery and the statistical procedure be applied to select the most likely sources. The measured parameters for these sources are compared visually to assure that no potential source is removed from consideration because of a measurement error. When the possibility of such an error has been eliminated, the identification can be made using the statistical procedure.

These two comparison systems were evaluated in their ability to identify an unknown with five combinations of the measured parameters. These combinations were: (A) sulfur, nitrogen, vanadium and nickel content and the hydrocarbon GLC profile, (B) the five parameters in A plus carbon isotopic composition, (C) the six parameters of B plus sulfur isotopic composition, (D) the six parameters of B plus the weight per cent saturates, aromatics and asphaltics and the carbon isotopic composition on these three fractions, and (E) the twelve parameters of D plus the sulfur isotopic composition. Neither the odd-even predominance ratio nor the sulfur GLC profile parameters have digital values associated with them and for this reason they were omitted from the evaluation studies.

Each of the five parameter combinations was evaluated with five "unknown" oils using both comparison systems. The five unknowns selected were:

a. Unknown 1 Chosen to resemble oil No. 54
b. Unknown 2 Chosen to resemble oil No. 10
c. Unknown 3 Measured values for oil No. 30
d. Unknown 4 Measured values for oil No. 65
e. Unknown 5 Average value of each parameter among all library oils

The values of the identification parameters for each of the five unknowns are listed in column 2 of Tables 11-15. The Qwick-Qwery ± values of allowed deviation are given in column 3. Potential crude oil sources and their parameters that are the most similar to the unknowns are listed in the remaining columns in the upper half of each table. The lower halves summarize the results of the two comparison systems for each of the five parameter combinations, i.e., the number of matched parameters for each potential source for Qwick-Qwery and the value of the discriminant variate for the statistical procedure.

The results of the evaluation can be summarized by the statement that each comparison system matched the unknowns 1 to 4 with the correct oil and that with one exception no other oils in the data library are matched close enough for a mistake in identification to occur. The one exception occurs with unknown 1, which although identified correctly as oil No. 54, is not significantly different from No. 53 (Table 11). For unknown 5, the average oil, none of the oils in the data library can be seriously considered as a potential source.

TABLE 11

COMPARISON OF UNKNOWN 1 WITH POTENTIAL SOURCES

Parameters	Unknown 1	Allowed Deviation (±)	Crude Oil Numbers 54	53	55	52	51	43	15	27
1. Sulfur, Wt. %	4.90	0.24	4.83	4.65	4.07	4.39	5.18	1.37	4.91	3.80
2. Nitrogen, Wt. %	0.20	0.10	0.24	0.20	0.16	0.24	0.14	0.21	0.11	0.20
3. Vanadium, Wt. ppm	55.7	5.0	58.9	52.4	43.2	82.9	92.0	57.1	15.6	73.3
4. Nickel Wt. ppm	63.5	5.0	66.9	60.2	38.5	39.8	25.2	31.5	14.1	23.8
5. HC GLC Profile	1	1	1	2	3	3	1	6	2	0
6. $\delta^{13}C$ - Total	-27.0	0.5	-26.7	-26.8	-26.6	-26.2	-25.8	-25.5	-25.3	-27.3
7. Saturates, Wt. %	26.5	2.0	27.3	26.4	30.5	24.9	25.4	42.6	26.2	33.0
8. $\delta^{13}C$ - Saturates	-28.0	0.5	-28.5	-28.0	-27.3	-28.0	-26.2	-26.3	-25.1	-28.0
9. Aromatics, Wt. %	63.0	2.0	62.9	65.8	61.2	60.6	66.9	47.7	64.1	57.6
10. $\delta^{13}C$ - Aromatics	-27.0	0.5	-27.4	-27.4	-27.2	-27.0	-26.5	-25.2	-25.2	-27.0
11. Asphaltics, Wt. %	9.5	2.0	9.8	7.8	8.3	14.5	7.7	9.7	9.7	9.5
12. $\delta^{13}C$ - Asphaltics	-27.0	0.5	-26.5	-27.3	-26.7	-27.2	-26.4	-26.0	-25.6	-27.4
13. $\delta^{34}S$	-14.0	1.5	-14.4	-14.2	-13.5	-14.3	-13.2	2.5	-7.1	-8.7

Qwick Qwery Comparison	Number of Parameters	Number of Matched Parameters 54	53	55	52	51	43	15	27
A. Parameters 1-5	5	5	4	1	1	2	3	3	2
B. Parameters 1-6	6	6	5	2	1	2	3	3	3
C. Parameters 1-6+13	7	7	6	3	2	3	3	3	3
D. Parameters 1-12	12	12	10	6	5	5	4	6	7
E. Parameters 1-13	13	13	11	7	6	6	4	6	7

Statistical Comparison	Number of Parameters	Discriminant Variate Value 54	53	55	52	51	43	15	27
A. Parameters 1-5	5	11	22	332	367	612	7854	7804	582
B. Parameters 1-6	6	12	22	334	374	628	7879	7836	583
C. Parameters 1-6+13	7	13	22	334	374	629	8181	7883	614
D. Parameters 1-12	12	20	36	362	408	690	8451	7989	656
E. Parameters 1-13	13	21	36	362	408	691	8753	8035	687

TABLE 12

COMPARISON OF UNKNOWN 2 WITH POTENTIAL SOURCES

Parameters	Unknown 2	Allowed Deviation (±)	Crude Oil Numbers							
			10	16	19	29	5	46	65	67
1. Sulfur, Wt. %	2.94	0.24	2.90	3.91	2.97	2.39	1.30	1.21	2.11	2.95
2. Nitrogen, Wt. %	0.19	0.10	0.18	0.22	0.10	0.09	0.26	0.23	0.09	0.14
3. Vanadium, Wt. ppm	12.0	5.0	11.2	14.4	12.4	10.0	18.8	39.0	14.0	25.6
4. Nickel, Wt. ppm	8.0	5.0	7.5	15.7	7.1	2.8	12.3	9.0	3.8	7.0
5. HC GLC Profile	2	1	1	1	2	1	6	10	6	1
6. $\delta^{13}C$ - Total	-28.4	0.5	-28.7	-25.5	-25.0	-26.6	-29.3	-27.1	-26.3	-26.6
7. Saturates, Wt. %	40.0	2.0	40.3	36.8	52.7	48.3	40.9	38.6	48.5	42.9
8. $\delta^{13}C$ - Saturates	-29.9	0.5	-30.2	-25.6	-25.1	-26.9	-30.4	-27.4	-26.7	-26.8
9. Aromatics, Wt. %	50.0	2.0	49.9	53.6	39.5	45.9	51.5	48.8	44.2	44.6
10. $\delta^{13}C$ - Aromatics	-28.8	0.5	-29.2	-25.2	-25.1	-26.3	-29.3	-27.8	-26.0	-26.2
11. Asphaltics, Wt. %	10.0	2.0	9.8	9.6	7.8	5.7	7.6	12.7	7.3	12.5
12. $\delta^{13}C$ - Asphaltics	-28.1	0.5	-28.4	-25.5	-25.0	-24.8	-29.4	-27.7	-26.3	-26.4
13. $\delta^{34}S$	-4.0	1.5	-4.3	-8.2	-9.6	-	-3.1	8.7	-8.3	-2.7
Qwick Qwery Comparison	Number of Parameters		Number of Matched Parameters							
A. Parameters 1-5	5		5	3	5	3	3	2	4	4
B. Parameters 1-6	6		6	3	5	3	3	2	4	4
C. Parameters 1-6+13	7		7	3	5	3	4	2	4	5
D. Parameters 1-12	12		12	4	5	3	7	5	4	4
E. Parameters 1-13	13		13	4	5	3	8	5	4	5
Statistical Comparison	Number of Parameters		Discriminant Variate Value							
A. Parameters 1-5	5		9	224	23	264	1993	4240	410	399
B. Parameters 1-6	6		10	317	151	300	2002	4258	459	435
C. Parameters 1-6+13	7		11	337	186	-	2003	4437	479	437
D. Parameters 1-12	12		14	777	942	694	2035	4351	809	693
E. Parameters 1-13	13		15	796	977	-	2036	4530	830	695

TABLE 13

COMPARISON OF UNKNOWN 3 WITH POTENTIAL SOURCES

Parameters	Unknown 3	Allowed Deviation (±)	Crude Oil Numbers				
			30	52	27	69	31
1. Sulfur, Wt. %	3.90	0.24	3.90	4.39	3.80	3.82	3.77
2. Nitrogen, Wt. %	0.23	0.10	0.23	0.24	0.20	0.18	0.13
3. Vanadium, Wt. ppm	83.3	5.0	83.3	82.9	73.3	63.4	47.9
4. Nickel, Wt. ppm	24.8	5.0	24.8	39.8	23.8	23.2	15.0
5. HC GLC Profile	5	1	5	3	0	0	0
6. $\delta^{13}C$ - Total	-26.6	0.5	-26.6	-26.2	-27.2	-26.9	-26.7
7. Saturates, Wt. %	36.7	2.0	36.7	24.9	33.0	32.4	38.7
8. $\delta^{13}C$ - Saturates	-27.2	0.5	-27.2	-28.0	-28.0	-27.0	-27.9
9. Aromatics, Wt. %	55.5	2.0	55.2	60.6	57.6	48.6	54.6
10. $\delta^{13}C$ - Aromatics	-26.9	0.5	-26.9	-27.0	-27.0	-26.8	-27.3
11. Asphaltics, Wt. %	8.1	2.0	8.1	14.5	9.5	19.1	6.7
12. $\delta^{13}C$ - Asphaltics	-26.9	0.5	-26.9	-27.2	-27.4	-27.1	-27.3
13. $\delta^{34}S$	-5.4	1.5	-5.4	-14.3	-8.7	-9.6	-9.6
Qwick Qwery Comparison	**Number of Parameters**		**Number of Matched Parameters**				
A. Parameters 1-5	5		5	2	3	3	2
B. Parameters 1-6	6		6	3	3	4	3
C. Parameters 1-6+13	7		7	3	3	4	3
D. Parameters 1-12	12		12	5	6	7	8
E. Parameters 1-13	13		13	5	6	7	8
Statistical Comparison	**Number of Parameters**		**Discriminant Variate Value**				
A. Parameters 1-5	5		0	69	148	323	1190
B. Parameters 1-6	6		0	71	152	324	1190
C. Parameters 1-6+13	7		0	158	164	344	1210
D. Parameters 1-12	12		0	285	182	512	1206
E. Parameters 1-13	13		0	373	194	532	1226

TABLE 14

COMPARISON OF UNKNOWN 4 WITH POTENTIAL SOURCES

Parameters	Unknown 4	Allowed Deviation (±)	Crude Oil Numbers					
			65	67	18	64	55	44
1. Sulfur, Wt. %	2.86	0.24	2.86	2.95	4.08	3.03	4.07	1.70
2. Nitrogen, Wt. %	0.12	0.10	0.12	0.14	0.13	0.19	0.16	0.17
3. Vanadium, Wt. ppm	23.9	5.0	23.9	25.6	19.3	49.0	43.2	85.5
4. Nickel, Wt. ppm	8.4	5.0	8.4	7.0	14.1	12.2	38.5	10.7
5. HC GLC Profile	4	1.0	4	1	2	2	3	4
6. $\delta^{13}C$ - Total	-26.6	0.5	-26.6	-26.6	-25.1	-26.9	-26.6	-26.3
7. Saturates, Wt. %	43.2	2.0	43.2	42.9	32.7	39.5	30.5	53.3
8. $\delta^{13}C$ - Saturates	-26.9	0.5	-26.9	-26.8	-25.3	-27.2	-27.3	-27.3
9. Aromatics, Wt. %	48.7	2.0	48.7	44.6	58.5	53.6	61.2	38.3
10. $\delta^{13}C$ - Aromatics	-26.2	0.5	-26.2	-26.2	-25.2	-26.9	-27.2	-26.1
11. Asphaltics, Wt. %	8.1	2.0	8.1	12.5	8.8	6.8	8.3	8.4
12. $\delta^{13}C$ - Asphaltics	-26.3	0.5	-26.3	-26.4	-25.7	-26.8	-26.7	-26.1
13. $\delta^{34}S$	-14.9	1.5	-14.9	-2.7	-6.0	-10.0	-13.5	6.6
Qwick Qwery Comparison	Number of Parameters		Number of Matched Parameters					
A. Parameters 1-5	5		5	4	2	3	2	3
B. Parameters 1-6	6		6	5	2	4	3	4
C. Parameters 1-6+13	7		7	5	2	4	4	4
D. Parameters 1-12	12		12	9	3	7	6	6
E. Parameters 1-13	13		13	9	3	7	7	8
Statistical Comparison	Number of Parameters		Discriminant Variate Value					
A. Parameters 1-5	5		0	47	356	544	684	1979
B. Parameters 1-6	6		0	47	380	545	684	1980
C. Parameters 1-6+13	7		0	211	468	572	685	2493
D. Parameters 1-12	12		0	83	631	594	1015	2193
E. Parameters 1-13	13		0	248	719	620	1018	2705

TABLE 15

COMPARISON OF UNKNOWN 5 WITH POTENTIAL SOURCES

Parameters	Unknown 5	Allowed Deviation (±)	Crude Oil Numbers 43	44	67	65	11
1. Sulfur, Wt. %	1.78	0.24	1.37	1.70	2.95	2.86	0.26
2. Nitrogen, Wt. %	0.18	0.10	0.21	0.17	0.14	0.12	0.08
3. Vanadium, Wt. ppm	34.8	5.0	57.1	85.5	25.6	23.9	1.07
4. Nickel, Wt. ppm	18.6	5.0	31.5	10.7	7.0	8.4	0.80
5. HC GLC Profile	4	1	6	4	1	4	10
6. $\delta^{13}C$ - Total	-26.7	0.5	-25.5	-26.3	-26.6	-26.6	-26.9
7. Saturates, Wt. %	50.4	2.0	42.6	53.3	42.9	43.2	50.3
8. $\delta^{13}C$ - Saturates	-27.4	0.5	-26.3	-27.3	-26.8	-26.9	-28.4
9. Aromatics, Wt. %	41.3	2.0	47.7	38.3	44.6	48.7	41.2
10. $\delta^{13}C$ - Aromatics	-26.6	0.5	-25.2	-26.1	-26.2	-26.2	-27.0
11. Asphaltics, Wt. %	8.3	2.0	9.7	8.4	12.5	8.1	8.5
12. $\delta^{13}C$ - Asphaltics	-26.2	0.5	-26.0	-26.1	-26.4	-26.3	-27.1
13. $\delta^{34}S$	-1.7	1.5	2.5	6.6	-2.7	-14.9	-1.8
Qwick Qwery Comparison	**Number of Parameters**		**Number of Matched Parameters**				
A. Parameters 1-5	5		1	3	1	2	1
B. Parameters 1-6	6		1	4	2	3	2
C. Parameters 1-6+13	7		1	4	3	3	3
D. Parameters 1-12	12		3	8	4	7	6
E. Parameters 1-13	13		3	8	5	7	7
Statistical Comparison	**Number of Parameters**		**Discriminant Variate Value**				
A. Parameters 1-5	5		453	928	687	662	286,787
B. Parameters 1-6	6		468	930	688	662	286,788
C. Parameters 1-6+13	7		488	1007	689	855	286,788
D. Parameters 1-12	12		607	951	779	774	286,810
E. Parameters 1-13	13		627	1027	780	967	286,810

The successful distinction of five Mississippi crude oils, Nos. 15-19, from one another was suggested as a rigorous test of any matching scheme (page 40-41). The statistical procedure based on the four elemental parameters achieved the unique distinction as demonstrated by the values of the discriminant variate when each oil source in turn is treated as the unknown (Table 16).

The statistical procedure was also evaluated on the basis of the efficiency of four, five and six parameters to distinguish among the crude oils in a 50 source library. Each of the oils were used, in turn, as an unknown to determine those sources that were not identified uniquely. Sources were considered non-unique when the value of the discriminant variate was less than 40 for four and five parameters and less than 20 for six parameters. The results are summarized in Table 17 for the three parameter combinations. The numerator in the fraction is the number of sources that are not uniquely identified from among the 50 sources. The efficiency of the sulfur isotopic composition as a diagnostic parameter is demonstrated by the fact that only four sources are not distinguished from all other sources. These four are two pair of crude oil sources, Nos. 59-60 and 62-63 from adjacent fields in Abu Dhabi and Israel. Each pair is distinguished from the other as well as from all other sources. The paired oils are indistinguishable and each pair should be considered a single source. For practical purposes this source library contains 48 unique sources based on these six identification parameters and 50 crude oil samples.

TABLE 16

COMPARISON OF MISSISSIPPI CRUDE OIL SOURCES

Parameters	Crude Oil Numbers 15	16	17	18	19
1. Sulfur, Wt. %	4.91	3.91	1.65	4.08	2.97
2. Nitrogen, Wt. %	0.11	0.22	0.06	0.13	0.10
3. Vanadium, Wt. ppm	15.6	14.4	<0.2	19.3	12.4
4. Nickel, Wt. ppm	14.1	15.7	2.0	14.1	7.1
5. HC GLC Profile	2	1	3	2	2
6. $\delta^{13}C$ - Total	-25.3	-25.5	-24.9	-25.1	-25.0
7. Saturates, Wt. %	26.2	36.8	62.2	32.7	52.7
8. $\delta^{13}C$ - Saturates	-25.1	-25.6	-25.2	-25.3	-25.1
9. Aromatics, Wt. %	64.1	53.6	35.7	58.5	39.5
10. $\delta^{13}C$ - Aromatics	-25.2	-25.2	-24.3	-25.2	-25.1
11. Asphaltics, Wt. %	9.7	9.6	2.1	8.8	7.8
12. $\delta^{13}C$ - Asphaltics	-25.6	-25.3	-24.4	-25.7	-25.0
13. $\delta^{34}S$	-7.1	-8.2	-9.4	-6.0	-9.6

Unknown Oil	Discriminant Variate Value*				
15	0	224	872,290	166	1060
16	181	0	740,381	103	350
17	2609	2059	0	2266	1390
18	159	145	1,335,119	0	651
19	596	239	545,145	386	0

*Discriminant variate determined using the four parameters: sulfur, nickel, vanadium and nickel contents.

TABLE 17

IDENTIFICATION EFFICIENCY OF SULFUR ISOTOPIC COMPOSITION

Parameters	4	5	6
	S	S	S
	N	N	N
	V	V	V
	Ni	Ni	Ni
	-	$\delta^{13}C$	$\delta^{13}C$
	-	$\delta^{34}S$	$\delta^{34}S$
Unidentified Sources	16/50	13/50	4/50

As pointed out in Appendix N, several assumptions and approximations are embodied in the statistical procedure because only one sample of each source was available. The validity of the assumptions and the consequence of the approximations could be established by measurement of the variations in the values of the proposed identification parameters that occur in the normal course of oil production from commercial crude oil sources.

SECTION IX

WEATHERING STUDIES

The demonstration of the feasibility to identify a crude oil based on a comparison of measured values for selected parameters has been made on crude oils which were not subjected to environmental conditions at an oil spill site.

The identification system takes evaporative weathering into account by measuring the parameters of the crude oil after it has been topped to 600°F to remove the volatile components. In an actual oil spill, however, in addition to evaporation, the characteristics of a crude oil could also change through bacterial degradation, photolysis, oxidation, and water solubility of some components. The influence of weathering on the identification parameters was studied by weathering experiments under simulated-ocean spill conditions.

Weathering Procedure

The weathering experiments were conducted in 2 x 4 foot galvanized metal tubs located on a building roof in the Phillips Research Center. The interior surfaces of the tubs were coated with an epoxy paint to eliminate any influence from the zinc galvanizing and to reduce corrosion. Approximately eight gallons of synthetic sea water (Instant Ocean from Aquarium Systems, Wickliffe, Ohio 44092) were placed in each tub. One end of the tub was filled with quartz river sand to give a small area above the water level to simulate a beach. To provide a marine coastal microbial culture, one quart of tidal flats mud from the Sorrento Valley estuary (California) was mixed into the sea water and allowed to settle overnight. From 500 to 800 ml of crude oil was poured onto the water surface. Initially the oil covered 1/3 to 1/2 of the water surface and after a week of outdoor exposure the water was completely covered with oil, but not uniformly. Air was bubbled through the water continuously to simulate wave action.

Two crude oils, Nos. 83 and 84, were weathered under simulated ocean conditions at ambient atmospheric conditions from August 10 to September 29, 1972. Crude oil No. 83 from Monagas, Venezuela formed a crusty, viscous coating on the water surface after the fourth day. After 49 days, the water surface was nearly free of oil; the oil residue had either sunk to the bottom or stuck to the walls of the tank. Crude oil No. 84 from Ecuador covered the water surface completely after several days with a fluid residue. The thickness of the oil layer depended upon the wind conditions, a thicker layer being produced at the downwind side of the tank.

Samples of the oil residue remaining on the water surface were taken after 1, 4, 8, 21 and 49 days. Each sample was refrigerated to solidify the oil and any water was removed by decantation. The oils were dissolved in toluene, and then topped by vacuum distillation to produce the 600^{+}F bottoms for measurement of the parameters. The values obtained are reported in Tables 18 and 19.

The values for the sulfur, nitrogen, nickel and vanadium concentrations as well as the carbon and sulfur isotopic compositions are within the range of values expected from variations in sampling, distillation and measurement and, therefore, were not effected by these weathering conditions. The GLC profiles and the values from the silica gel separation are affected and thus are of decreased value in oil source identification. With each oil, the asphaltics content nearly doubles during the course of the weathering. The loss of the lower boiling components, i.e., saturates and aromatics, is shown by changes in the front end of the GLC profiles. Initially, for the Ecuador crude oil,

TABLE 18

EFFECT OF WEATHERING CRUDE OIL NO. 83, MONAGAS PIPELINE CRUDE OIL, VENEZUELA

	Days Weathered					
Parameter	0	1	4	8	21	49
Sulfur, Wt. %	2.4	2.4	2.5	2.5	2.5	2.6
Nitrogen, Wt. %	0.48	0.53	0.57	0.65	0.59	0.54
Nickel, ppm	70	84	81	86	75	76
Vanadium, ppm	232	256	244	254	249	241
Saturates, Wt. %	30.3	29.9	28.7	27.6	25.8	26.8
Aromatics, Wt. %	53.5	50.9	48.9	44.7	43.8	45.3
Asphaltics, Wt. %	16.2	19.2	22.4	27.7	30.4	27.8
$\delta^{13}C_{PDB}$, °/oo						
a) 600^{+}F Residue	-27.0	-27.1	-27.9	-28.5	-27.4	-27.1
b) Saturates	-27.8	-27.6	-27.6	-27.5	-27.2	-27.6
c) Aromatics	-27.1	-27.3	-26.8	-27.2	-27.2	-27.3
d) Asphaltics	-27.3	-26.8	-27.4	-27.4	-27.2	-27.3
$\delta^{34}S_{CDM}$, °/oo	7.6	6.5	7.2	-	-	7.4
GLC Profile	10	10	10	10	10	10

TABLE 19

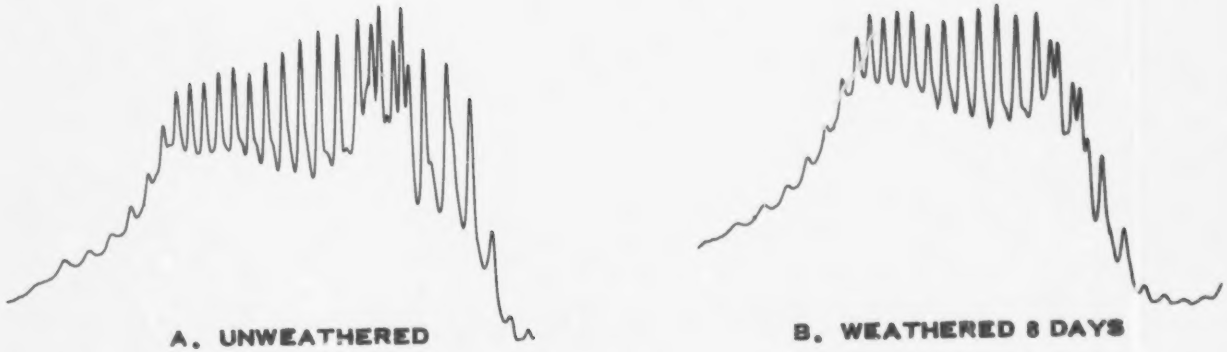
EFFECT OF WEATHERING CRUDE OIL NO. 84, ECUADOR COMPOSITE CRUDE

Parameter	Days Weathered 0	1	4	8	21	49
Sulfur, Wt. %	1.2	1.0	1.1	1.1	1.2	1.3
Nitrogen, Wt. %	0.28	0.25	0.28	0.32	0.33	0.35
Nickel, ppm	29	36	39	37	37	36
Vanadium, ppm	73	69	79	70	85	83
Saturates, Wt. %	35.2	45.9	40.3	43.2	39.9	32.1
Aromatics, Wt. %	53.3	42.5	47.8	42.3	41.0	47.6
Asphaltics, Wt. %	11.5	11.6	11.9	14.5	19.1	20.3
$\delta^{13}C_{PDB}$, °/oo						
a) 600$^+$F Residue	-25.8	-26.1	-26.1	-26.3	-26.1	-26.2
b) Saturates	-27.6	-27.8	-27.5	-27.4	-27.3	-27.3
c) Aromatics	-25.9	-26.0	-25.4	-25.4	-25.3	-25.6
d) Asphaltics	-25.3	-25.5	-25.6	-25.4	-25.9	-25.7
$\delta^{34}S_{CDM}$, °/oo	- 1.6	-	-	-	-	- 2.0
GLC Profile	6	9	6	9	7	9

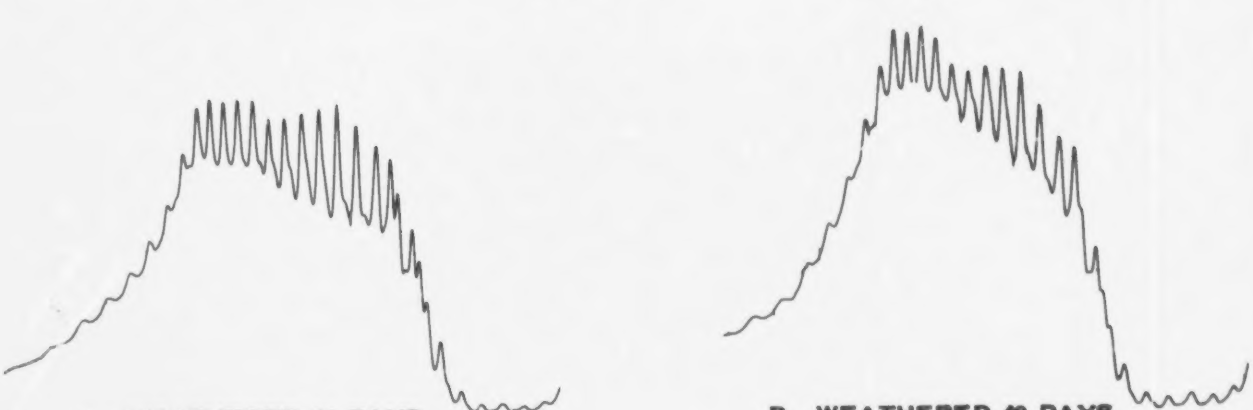
the GLC profile on the 600^{+}F bottoms contains large peaks for the normal paraffins C_{14} - C_{18}. After 49 days of weathering the C_{14} and C_{15} peaks are reduced to a small fraction of their initial size and the C_{16} - C_{17} peaks are reduced significantly as is the envelope under the paraffin peaks through C_{25} (Figure 9). The heavier Monagas Venezuelan crude oil also loses the lighter ends during weathering (Figure 10). The area between the two curves represents the material lost during weathering. The OEP curves for the Ecuador crude oil samples did not change significantly as a function of weathering time. The decrease in concentration of both saturates and aromatics indicates that an evaporative mechanism is causing most of the changes rather than microbial action. Bacterial degradation is expected to affect only the n-paraffins.

The enrichment of the heavier end of the 600^{+}F bottoms (Ecuador) at the expense of the lighter ends during weathering is illustrated by the data in Table 20. The lighter normal paraffins C_{14} - C_{16} decreased from a total of 9.2 per cent of the total paraffins (C_{13} - C_{38}) to about 1.0 per cent during the 49 days of weathering. The Venezuelan crude oil contains too small an amount of n-paraffins to be measured by the techniques employed. This fact itself is sufficient to distinguish this crude oil from the majority of those in our survey.

The infrared spectra of the weathered samples after distillation indicated a progressive small increase in hydroxyl, -OH, and carbonyl, $>C = O$, absorptions with the duration of weathering. Oxidation of crude oil residues is expected under our weathering conditions and the observed infrared spectra confirm this. The variations in the spectra of the two unweathered 600^{+}F bottoms are insufficient to distinguish between them.


A. UNWEATHERED

B. WEATHERED 8 DAYS


C. WEATHERED 21 DAYS

D. WEATHERED 49 DAYS

FIGURE 9 - EFFECT OF WEATHERING ON GLC PROFILE, 600^{+}F BOTTOMS OF ECUADOR CRUDE OIL

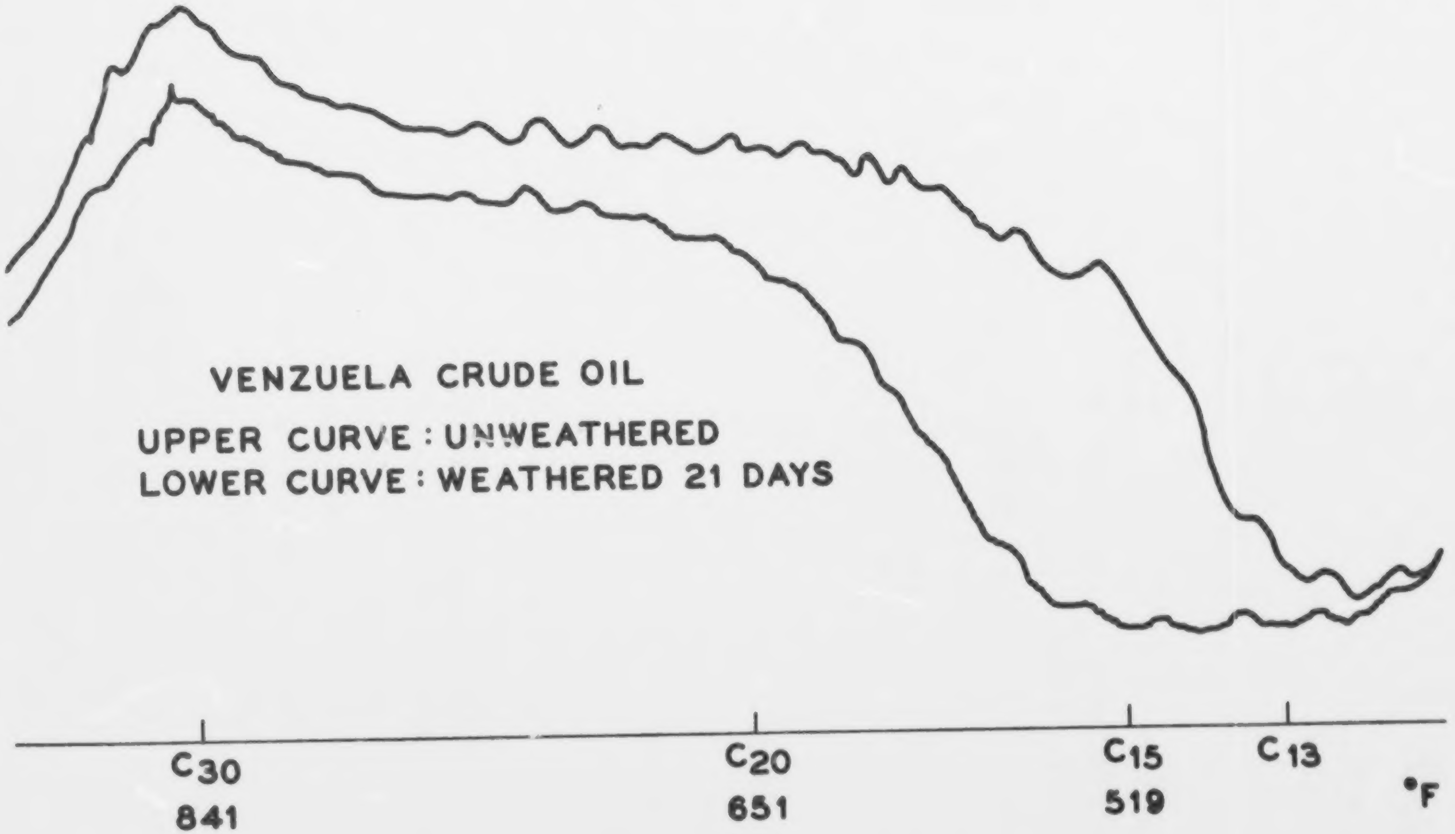


FIGURE 10 - EFFECT OF WEATHERING ON GLC PROFILE (600^{+}F BOTTOMS)

TABLE 20

EFFECT OF WEATHERING ON RELATIVE NORMAL PARAFFIN CONTENT

	Relative Normal Paraffin Content, Wt. %*								
Carbon Number	14	15	16	17	18	32	34	36	38
Days Weathered									
0	2.0	3.1	4.1	5.9	6.0	2.4	1.5	0.8	0.6
1	1.6	3.0	4.1	5.8	6.0	2.5	1.4	0.8	0.7
4	0.8	2.0	3.3	5.0	5.3	2.8	1.7	0.9	0.7
8	0.2	1.3	3.0	5.4	6.0	2.5	1.4	0.7	0.6
21	0.05	0.3	1.8	5.1	6.3	3.1	2.1	1.1	0.9
49	0.04	0.1	0.9	3.8	5.5	4.2	3.0	1.8	1.7

*The normal paraffins that are recovered by urea adduction of the saturates fraction are measured by gas liquid chromatography. The relative concentrations are calculated by normalization of paraffins in the C_{13} - C_{38} range to 100%.

This weathering study demonstrates that the four elemental contents: sulfur, nitrogen, vanadium and nickel, and the carbon and sulfur isotopic compositions are stable to weathering when the measurements are made on a 600$^+$F bottoms. The other parameters are affected by weathering and their application to source identification is limited by the extent of weathering.

SECTION X

SUMMARY DISCUSSION

A comprehensive multiparameter oil pollution source identification system utilizing 15 diagnostic parameters is presented. The results of measuring these 15 parameters on eighty crudes is presented. The effect of weathering crude oils in a simulated ocean environment is described. Two computerized procedures for comparing the parameters of an unknown oil with the parameters of the eighty crude oils are also presented.

A prime objective of any passive tagging system is the elimination of weathering as a variable in the identification of pollutants and their source. This can be accomplished by either measuring parameters that are unaffected by weathering or by subjecting both weathered and unweathered samples to a procedure designed to minimize or eliminate any changes in samples caused by weathering. If subjected to oil spill conditions, the properties of crude oils will begin to change immediately due to evaporation and dissolution of lighter components. The elemental analysis parameters are likely to change during weathering because components containing heteroelements, S, N, V, and Ni, will tend to be associated with the heavier components, thus their effective concentration will increase as weathering progresses. Analogous effects will also be noted with other parameters. Other changes may be observed due to microbial action, photolysis, and oxidation effects that occur during extended weathering.

The measurement of the parameters on the 600^{+}F bottoms prepared from the crude oil samples represents a realistic approach to eliminating weathering effects. Both weathered and unweathered oils are reduced to a common base on which measured parameters are directly comparable. The adoption of 600^{+}F bottoms (rather than some other temperature) as the material on which to measure parameters represents an arbitrary choice. As noted in Section IV and IX, some changes in the GLC profiles, silica gel fractions, and OEP curves do occur during weathering. These changes might be minimized by measurement of parameters on bottoms having a higher initial boiling point such as the 650^{+}F bottoms recommended by the Institute of Petroleum.[11] Such a change in procedure should be carefully considered to assess the influence of hydrocarbon cracking at the higher temperature involved.

Although the GLC profile is excluded as one of the quantitative identification parameters because of weathering, the GLC profile can serve as a preliminary screening measurement to establish whether an unknown is derived from a refined product or a crude oil. The GLC profile variation for the 600^{+}F bottoms is sufficient to eliminate some potential sources, even with weathered samples. For example, those profiles exhibiting strong n-paraffin peaks are distinguished from those having small or no n-paraffin peaks, i.e., Section VII, Figure 6, page 47. The loss of the lighter n-paraffin by evaporation does not invalidate the distinction.

The sulfur, nitrogen, vanadium, and nickel content parameters have a sufficiently wide range of values to be useful in distinguishing among oil sources. No significant changes in values are noted in weathering studies. In many instances, these four parameters alone are sufficient to distinguish among many potential oil sources. These parameters are easily measured in most laboratories.

The carbon and sulfur isotopic composition parameters strengthen the identification system, since each exhibits a range of values and remains unchanged during weathering. This measurement requires an isotope-ratio mass spectrometer facility including the combustion-purification trains to prepare samples for measurement.

It is possible to distinguish among most oil sources on the basis of these seven parameters. In cases where further corroboration is required, the sulfur GLC profile and fractions by silica gel separation for additional measurements can be obtained.

The sulfur GLC profiles and OEP curves of crude oils each represent parameters that have a high potential for being able to distinguish among sources. At this point, however, the utilization of these data requires manual comparison and is thus time consuming and subject to human error. Transformation of the data into a form compatible with computerized analysis appears justified. Improved handling of the hydrocarbon GLC profile data may permit their quantitative application.

The use of V/Ni ratios as an identification has been suggested.[4,5] In addition, S/N, V/S, V/N and other ratios might be considered. In some situations, a ratio, such as the V/Ni ratio, may provide some identification potential since change occurring in crude oils during weathering may affect the individual concentrations without changing ratios. In these cases, the ratio is independent of the concentrations and represents a useful identification parameter.

The use of all the reported values based on the silica gel separations, even in the absence of weathering, does not improve the identification potential enough to justify the effort expended. The large variations noted in the amount of asphaltic fraction are of potential value. Additional work to obtain this fraction, or a comparable fraction, in a less time consuming process might be justified. Although the OEP curves are potentially useful, studies to obtain the needed information with less effort are warranted.

Three different comparison techniques have been used in evaluating the identification techniques. These are a direct manual comparison and the computer-based Qwick-Qwery and statistical comparison procedures. Each of these techniques has merit for particular applications. The best system will utilize a combination of these approaches.

Practical Evaluation of the Proposed System

The proposed system was tested on "real" samples that were obtained from the Oil Spill Branch, Office of Research and Monitoring, Environmental Protection Agency, Edison, New Jersey. Twelve crude oils and two weathered residues were received. The weathered residues were known to have originated from among the twelve crude oils. Nine parameters were measured on each crude oil source sample oils. but only four parameters could be measured on the weathered residues because of the small samples obtained (2-3 ml). All the measurements were made on 600^{+}F bottoms. The data are presented in Table 21. The crude oils are numbers 85 through 96, inclusive, and the weathered residues are numbers 99 and 100. Direct comparison of the data indicates that oils 86 and 93 are nearly identical as are oils 94 and 95. Oils 85 and 89 are similar but the agreement is not as good.

The weathered (16 days) residue No. 99 matches oils 86 and 93 based on the sulfur content alone. The vanadium and nickel contents agree also. No further identification parameters are necessary to match this weathered residue with the two low-sulfur crude oils in this 12-source library. The weathered (2 days) residue No. 100 may have originated from oil 96 based on direct comparison of the sulfur,

TABLE 21. SUMMARY OF VALUES ON EPA CRUDE OILS AND WEATHERED SAMPLES

EPA Crude Oil Number	600^+F Residue Wt. %	Sulfur Wt. %	Nitrogen Wt. %	Vanadium Wppm	Nickel Wppm	GLC Profile	δ^{13}C o/oo	Silica Gel Fractions, Wt. %		
								Saturates	Aromatics	Asphaltic
85	71.1	1.73	0.26	167	20.4	3	-26.6	31.2	60.9	8.0
86	60.4	0.27	0.17	1.0	7.0	1	-26.6	39.3	57.3	3.4
87	73.4	1.27	0.26	87.7	40.7	8	-26.7	34.0	59.6	6.4
88	68.2	2.01	0.25	55.3	16.4	2	-26.6	46.0	48.3	5.5
89	67.9	1.60	0.25	147	17.4	6	-26.6	38.4	54.6	7.0
90	77.1	1.66	0.24	198	17.3	0	-26.5	41.3	53.9	4.8
91	78.1	1.30	0.28	90.8	23.4	8	-27.6	33.7	59.0	7.3
92	73.1	1.45	0.25	129	16.6	0	-26.2	32.2	61.7	6.1
93	68.6	0.24	0.17	0.9	6.3	1	-26.5	34.6	59.0	6.4
94	61.1	1.19	0.07	0.4	0.7	3	-25.8	41.2	54.7	4.2
95	59.7	1.18	0.07	0.3	1.0	3	-25.8	42.6	54.0	3.4
96	79.8	2.04	0.29	250	26.5	8	-26.5	28.6	62.8	8.6
99 Weathered Residue		0.31	-	1(1)	9(1)	9	-26.6	-	-	-
100 Weathered Residue		2.03	-	200(1)	25(1)	9	-26.8	-	-	-

(1) Small sample did not permit highest accuracy.

vanadium and nickel contents. On the basis of the data oils 85, 89 and 90 are also potential sources. The small amount of weathered residues that were available prevented the vanadium and nickel measurements with the normal precision and accuracy. The uncertainty of these values reduces the confidence in the match.

The agreement in the carbon isotopic composition between the weathered residues and the potential sources confirm the tentative assignments. Nine of the 12 crude oil sources have equivalent carbon isotopic values. The values for oil Nos. 94 and 95 agree with one another and differ from the others. The value for oil 91 suggests that it is from a different geologic origin than the others.

The statistical comparison method was also applied to identification of these weathered residues. Each of the twelve sources was treated as an unknown to test for equivalency of sources. Two pair of oil sources, Nos. 86-93 and 94-95, were found to be equivalent and another pair 85-89 are probably equivalent. Therefore, there are only 10 distinctly different sources and possibly only 9.

The weathered residue No. 99 was matched statistically with the source pair 86-93. The value of the discriminant variate was 266 for this source. This value is larger than normally considered for a match. However, with the knowledge that the unknown was derived from this library, it is concluded that the match is the best possible. The next closest match, oil pair 94-95, had a discriminant variate of 3198.

Positive identification of oil 100 was not feasible based on the discriminant variate values:

Source Oil Number	Discriminant Variate
96	182
85-89	331
90	405

Although the most likely source, No. 96, is the same as selected by manual comparison of the data, the statistical procedure does not allow a firm conclusion to be reached.

The Environmental Protection Agency confirmed our identification that the weathered oil 99 was derived from source oil 93, which is identical to 86. The weathered oil 100 was derived from source oil 90, which is one of the three potential sources selected. Those two examples demonstrate the application of the proposed identification system to a real situation in which several suspect sources are nearly equivalent and small unknown samples are available. In both cases the number of potential sources was reduced to the point where other circumstantial evidence is needed.

SECTION XI

ACKNOWLEDGMENTS

The results and conclusions reported herein are possible only through the assistance and cooperation of professional associates and fellow employees. Their guidance, advice and interest from conception to completion of the study is deeply appreciated and is hereby acknowledged.

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SECTION XII

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SECTION XIII

APPENDICES

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APPENDIX A

PHILLIPS PETROLEUM COMPANY - METHOD 7128-AH-1*

PREPARATION AND DETERMINATION OF 600^{+}F BOTTOMS FROM CRUDE OIL

I. SCOPE

This method is for the preparation and determination of 600^{+}F bottoms from crude oil. These bottoms are characterized by measurements of selected properties useful in oil pollution source identification.

II. OUTLINE OF METHOD

A sample of crude oil which has been equilibrated at room temperature is topped under vacuum in a distillation apparatus to an end point of 214 F (101 C) and 0.15 mm Hg pressure. The residual oil is weighed and the per cent bottoms calculated. The 600^{+}F bottoms are collected for additional measurements.

III. APPARATUS

(a) Centrifuge. A Sorvall Superspeed RC2-B modified for operation at temperatures above ambient, made by Ivan Sorvall, Inc., Newtown, Connecticut, or equivalent. Teflon-lined centrifuge tubes, 50 ml, with caps.

(b) Pan Balance.

(c) Distillation Unit, Figure 1.

1. Round bottom distillation kettle, 500 ml, two-necked.
2. Thermometer, -10 to 250 C.
3. Delivery Tube.
4. Receiver.
5. Dewar Flask.

(d) Vacuum System, Figure 1.

1. Megavac Pump, 35 liters per minute.
2. High Vacuum Surge Tank.
3. Controlled Vacuum Surge Tank.

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*Issued: December 15, 1971
Revised: June 8, 1972

4. Solenoid Valve, Normally Open.

5. Compound Gauge, 30 psi to 30 inch vacuum.

6. McLeod Gauge.

7. Mercury Regulator Switch.

8. Relay Switch.

(e) Variac.

(f) Heating Mantle. Glascol Hemisphere.

IV. REAGENTS AND MATERIALS

(a) Sodium Sulfate, Anhydrous.

(b) Water Soluble Vacuum Grease. Mix 30 g glycerin, 30 g d-mannitol, 30 g d-sorbitol and 10 g of water. Heat and stir at a low temperature until the solution is clear. Cool rapidly with beating to induce fine crystal formation and to yield a smooth cream.

(c) Benzene.

(d) Acetone.

(e) Dichloromethane.

(f) Liquid Nitrogen.

(g) Boiling Sticks.

(h) Glass Wool.

V. PROCEDURE

(a) Sample Preparation.

The crude oil sample should be equilibrated at room temperature and well mixed before sampling. Pour about 35 ml of crude oil sample into each of four Teflon-lined centrifuge tubes containing about 1 gram of anhydrous sodium sulfate. Adjust the weight of each filled centrifuge tube and cap so that they all weigh the same (±0.1 g). This may be done by adding or removing sample. Place caps on tubes. The tubes must be balanced in order to be used in the high speed centrifuge. Centrifuge the sample at 20,000 rpm for 90 minutes at 30 C.

Transfer the centrifuged crude oil sample (4 tubes) into a tared distillation kettle. During the transfer avoid adding any of the material settled out at the bottom of the centrifuge tube. Reweigh the distillation kettle and add a boiling stick.

(b) Distillation.

1. Preparation of Vacuum System. Using Figure 1 as a guide, adjust the following valves as described:

   (a) Rotate the regulator until contact is made between the mercury column and the wire electrode.

   (b) Activate the relay to close the solenoid valve.

   (c) Open Valve 3, open Valve 4, and open Valve 2.

   (d) Close Valve 1 and close Valve 5.

   (e) Turn on vacuum pump.

2. Preparation of Distillation Unit. Connect the receiver, delivery tube and distillation kettle together as shown in Figure 1 using water-soluble grease on all glass joints. Open stopcock of the receiver and open Valve 5 so that a flow of nitrogen may displace the air in the system and be vented out the thermometer well opening. After a couple of minutes of purging, add liquid nitrogen to the Dewar flask and continue the nitrogen purge for 3 more minutes. Close Valve 5 and insert the thermometer into the well using water-soluble grease on the joint. Activate the relay switch to pull a partial vacuum on the system through the control vacuum surge tank. Place the heating mantle under the kettle and insulate the kettle and neck with glass wool. Leave an opening so that the inside of the kettle may be seen with the aid of a flashlight. Set the variac at 50 and reduce the pressure inside the system slowly by activating the relay. As the temperature increases and the pressure decreases, boiling will increase. Do not allow the sample to "bump" over into the receiver by reducing the pressure too rapidly. If necessary, nitrogen may be admitted into the system through Valve 5 to increase the pressure. Do not let boiling stop, however, or bumping is apt to occur on start up. When the pressure is reduced sufficiently, the McLeod gauge may be used to measure the pressure. Near the end point it is necessary to open Valve 1 to obtain a "hard" vacuum. The end point is reached at 214 F (101 C) and 0.15 mm Hg when boiling virtually ceases and no further distillate is collected.

   When the end point is reached, close Valve 1 and activate the relay. Admit nitrogen into the system slowly by opening Valve 5. When the system is at atmospheric pressure, remove the thermometer and remove the distillation kettle from the delivery tube. Wipe off the stopcock grease and weigh the distillation kettle.

Transfer 1-2 grams of the 600^{+}F bottoms to a small vial and seal under nitrogen. Store these vials at 40 F. Transfer the remaining 600^{+}F bottoms to a clean wide-mouthed sample jar.

Glassware is cleaned by rinsing with dichloromethane, benzene, water, and acetone and drying in an oven.

VI. CALCULATION

$$\text{Weight per cent bottoms } (600^{+}\text{F}) = \frac{\text{grams residue} \times 100}{\text{grams sample}}$$

APPENDIX A

PHILLIPS PETROLEUM COMPANY – METHOD 7128–AH

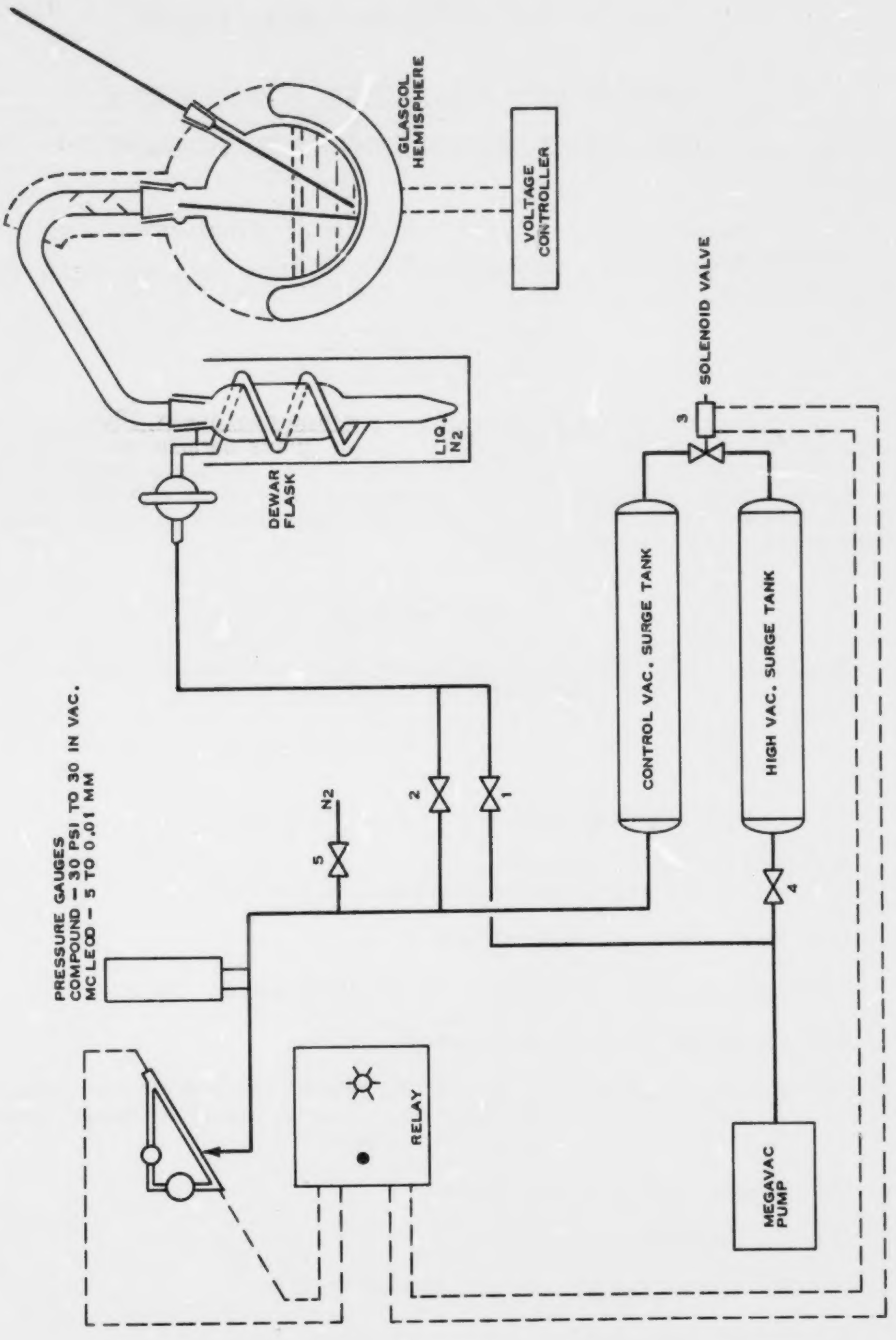
GLASCOL HEMISPHERE
VOLTAGE CONTROLLER
SOLENOID VALVE
3
LIQ. N_2
DEWAR FLASK
CONTROL VAC. SURGE TANK
HIGH VAC. SURGE TANK
1
2
4
5
N_2
PRESSURE GAUGES
COMPOUND – 30 PSI TO 30 IN VAC.
MC LEOD – 5 TO 0.01 MM
RELAY
MEGAVAC PUMP

FIGURE 1
SCHEMATIC DIAGRAM OF APPARATUS

APPENDIX B

PHILLIPS PETROLEUM COMPANY - METHOD 7234-AN*

DETERMINATION OF TOTAL NITROGEN IN 600^+F BOTTOMS FROM CRUDE OIL BY MICRO DUMAS-GAS CHROMATOGRAPHY

I. SCOPE

This method is for determination of 0.03 per cent and higher concentrations of total nitrogen in 600^+F bottoms from crude oil.

II. OUTLINE OF METHOD

A weighed sample is placed in a pyrolysis-combustion tube and is oxidized in an atmosphere of helium and oxygen. Water and carbon dioxide are removed by trapping at liquid nitrogen temperature. Nitrogen oxides are reduced to nitrogen with hot copper. The nitrogen is collected on molecular sieve at liquid nitrogen temperature and is determined quantitatively by gas chromatography using thermal conductivity detectors.

III. APPARATUS

1. Micro Dumas - Gas Chromatography Apparatus. A schematic diagram is shown in Figure 1. The basic components of this apparatus are:

    (a) Combustion Tube. Quartz, 30 in. long x 1/2 in. O.D. with 2 mm wall thickness.

    (b) Furnace. Electric, 900 C, for combustion tube.

    (c) U-Tube. Pyrex, heavy-wall, 22 in. long x 1/2 in. O.D. Filled with copper and heated to 550 C by electric furnace.

    (d) Trap for CO_2 and H_2O. Glass, 25 ml.

    (e) Nitrogen Trap. Attached to Perkin-Elmer valve. See Figure 2.

    (f) Manometer. Dual, 30-in., mercury-filled.

    (g) Constant Temperature Bath. E. H. Sargent Co. S-84810 except bath made of stainless steel and insulated. General Electric Company silicone fluid SF 96 (100) used as bath liquid.

    (h) Column. 13X Molecular Sieve.

    (i) V-F Converter. Vidar 240.

    (j) Electronic Counter. Hewlett Packard 5512A.

    (k) Bridge Power Supply. Applied Automation Model 11.

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*Issued: December 20, 1972.

(l) Thermistors. Fenwal G-112; Fenwal Electronics, Inc., Framingham, Mass.

(m) Pressure Regulator, Sub-Atmospheric. Moore Model 43; Moore Products Co., Spring House, Pa.

2. Auxiliary Apparatus

   (a) Combustion Boats. Platinum, 39 mm long.

   (b) Balance. Six-place, fast-weighing.

   (c) Dewar Flasks.

   (d) Pipets. Pasteur, disposable.

   (e) Spatula. Micro.

IV. REAGENTS AND MATERIALS

1. Acetanilide. N.B.S. No. 141 b; National Bureau of Standards, Washington, D. C.
2. Cuprin. A specially sized and treated metallic copper. Fisher Scientific Co. 13-109-10.
3. Cuprox. A specially sized and treated copper oxide. Fisher Scientific Co. 13-109-15.
4. Helium.
5. Liquid Nitrogen.
6. Molecular Sieve. 13X, screen 12/30; Coast Engineering Co., Redondo Beach, California.
7. Oxygen. Ultra high purity; Matheson Co., Inc., Joliet, Illinois.
8. Quartz Wool.
9. Silver Gauze. Approximately 80 mesh.

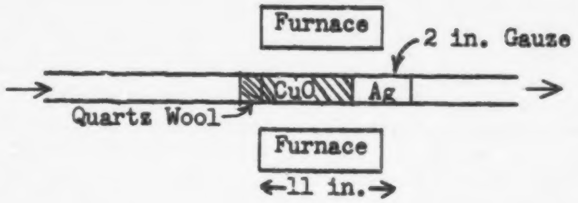
V. PROCEDURE

1. Preparation of Apparatus

Set up the apparatus as shown in Figure 1.

(a) Prepare purification traps 21 and 22 from 5 ft. of 1/4 in. copper tubing filled with 13X molecular sieve. Use silver gauze to hold the sieve in place.

(b) Add silver gauze and Cuprox to the quartz combustion tube as shown below.



(c) Fill the pyrex U-tube with Cuprin so that all of the Cuprin is in the furnace zone when the tube is in place. Use quartz wool plugs to hold the filling in place.

(d) Prepare and attach the nitrogen trap as shown in Figure 2. The trap is made of 1/4-in. stainless steel tubing.

(c) Add 13X molecular sieve to 5 ft. of 1/4-in. copper tubing and 6 in. of charcoal to the outlet end. Use silver gauze to hold the material in place. This column is shown in Figure 1 as 10.

2. Determination of Blank

After the apparatus is set up as shown in Figure 1, adjust the column helium flow as shown. Adjust the combustion helium flow to a fast rate (~100 cc/minute). After 10 minutes, place Dewar flasks filled with liquid nitrogen under traps 21, 22, and 6. After 15 minutes, place Dewar flask filled with liquid nitrogen under trap 8. Wait 2 minutes and adjust the combustion helium flow to 1 cc/minute. Adjust the oxygen flow to 1 cc/minute. Light the gas burner and slowly move the burner down the combustion tube to the electric furnace. (Approximate burn time is 20 minutes.) Turn off the burner, turn off the oxygen, and increase the combustion helium flow to about 100 cc/minute. Sweep the system for 15 minutes. Turn trap 8 to the inject position. Adjust inlet column helium pressure to 20 psig with valve 19 and indicate by marking on the manometer so that this pressure setting may be repeated. Adjust the outlet column helium pressure with valve 15 so that the outlet pressure is 5 mm below atmospheric pressure. Indicate on the manometer by marking so that this pressure setting may be repeated. Adjust the bridge circuit so that a very slow count is indicated on the electronic counter. Remove the Dewar flask containing liquid nitrogen from nitrogen trap 8 and replace with a Dewar flask containing water at room temperature. Record the number of counts produced by the nitrogen peak. Turn the trap to the collect position. Determine blanks periodically in order to get a representative value.

NOTE: Blank determinations should represent less than 100 micrograms of nitrogen.

3. Preparation of Calibration Curve

Weigh 1, 3, 5, 10, 20 mg (6-place balance) of acetanilide (NBS) in separate platinum boats. Place a piece of dry ice on top of the combustion tube in the area where the sample boat is to be placed. This cools the tube to eliminate evaporation of the sample during the sweep time. Place the sample boat in the combustion tube and sweep the system for 15 minutes with helium at 100 cc/minute to remove air. Place a Dewar flask containing liquid nitrogen under nitrogen trap 8. Wait 2 minutes and adjust the combustion helium flow to 1 cc/minute. Adjust the oxygen flow to 1 cc/minute. Remove the dry ice from the tube. Light the burner and slowly move the burner toward the sample. The sample is volatilized and oxidized. Since excess oxygen is removed by the copper U-tube, the amount of oxygen added to the combustion system is regulated depending on the amount and type of sample being analyzed. If samples are volatilized too rapidly, incomplete combustion products are formed on the outlet end of the combustion tube. After sample combustion is complete (ash may be present in the boat), turn the oxygen flow off. Increase the combustion helium flow to 100 cc per minute and sweep for 15 minutes. Inject and read the number of counts produced by the nitrogen peak as described in 2. Determination of Blank.

Calculate a factor (F) for each of the standard samples from the following formula.

$$F = \frac{\text{mg acetanilide, NBS x per cent nitrogen in acetanilide}}{(\text{counts - blank counts})\ 100}$$

Plot F vs net counts for each standard. Draw a curve through the points which best fits the points.

4. Analysis of Sample

Weigh about 0.5 gram of sample in a tared platinum boat. Place the boat in the cooled combustion tube and proceed to sweep, combust, sweep, inject and read the number of counts produced by the sample as described in Sections 2 and 3 above. At the end of the day, remove trap 6 and discard the water and CO_2.

NOTE: The combustion tube and U-tube usually last 2 days under constant use.

VI. CALCULATIONS

Calculate the nitrogen concentration in the sample as follows:

$$\text{Nitrogen, Wt. \%} = \frac{FN}{10\ W}$$

where:

F = Factor read from calibration curve corresponding to net counts of sample.
N = Net counts of sample.
W = Grams of sample.

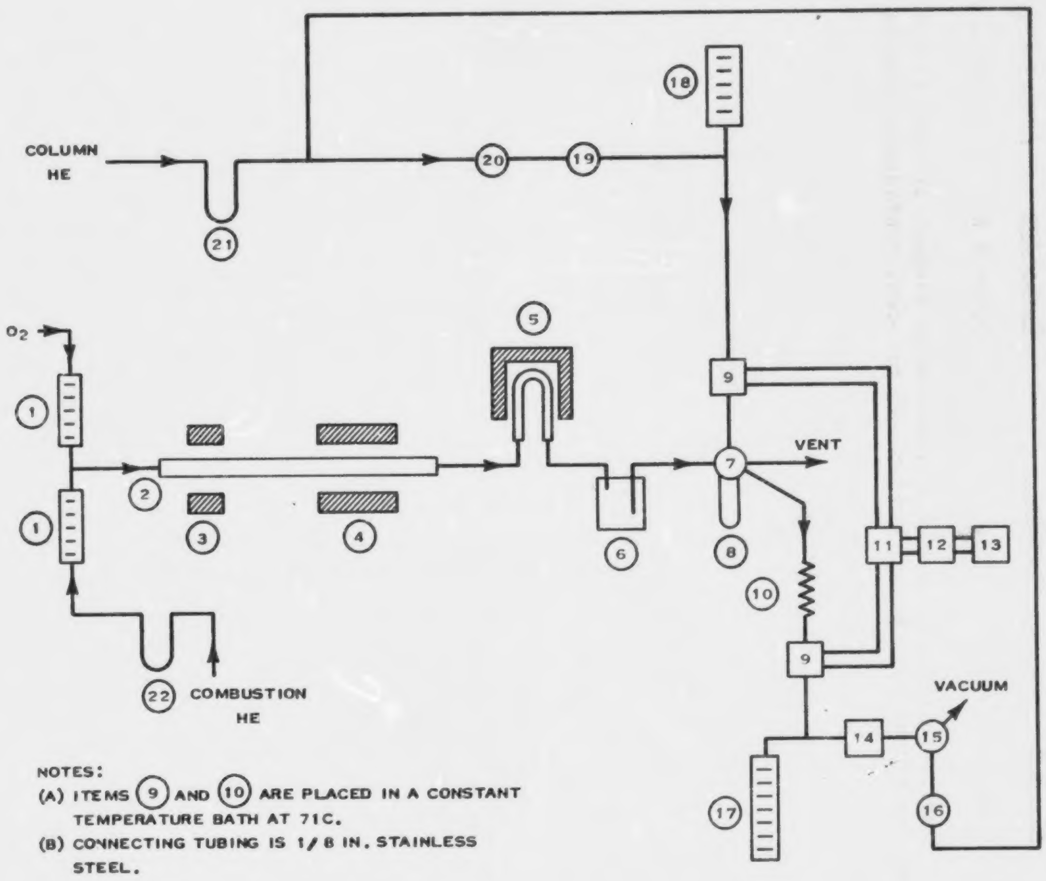
VII. PRECISION

A statistical evaluation of data from duplicate determinations on twelve samples showed:

Range, Wt. % N	Degrees of Freedom	Standard Deviation	Repeatability
0.03 to 0.7	12	0.019 % N	0.061 % N

Duplicate results should be considered suspect if they differ by more than the repeatability value shown (95 per cent confidence level).

PHILLIPS PETROLEUM COMPANY
METHOD 7234-AN


COLUMN HE
21
20
19
18
O2
1
2
3
4
5
6
7
8
VENT
9
10
11
12
13
VACUUM
14
15
16
17
22
COMBUSTION HE

NOTES:
(A) ITEMS ⑨ AND ⑩ ARE PLACED IN A CONSTANT TEMPERATURE BATH AT 71C.
(B) CONNECTING TUBING IS 1/8 IN. STAINLESS STEEL.

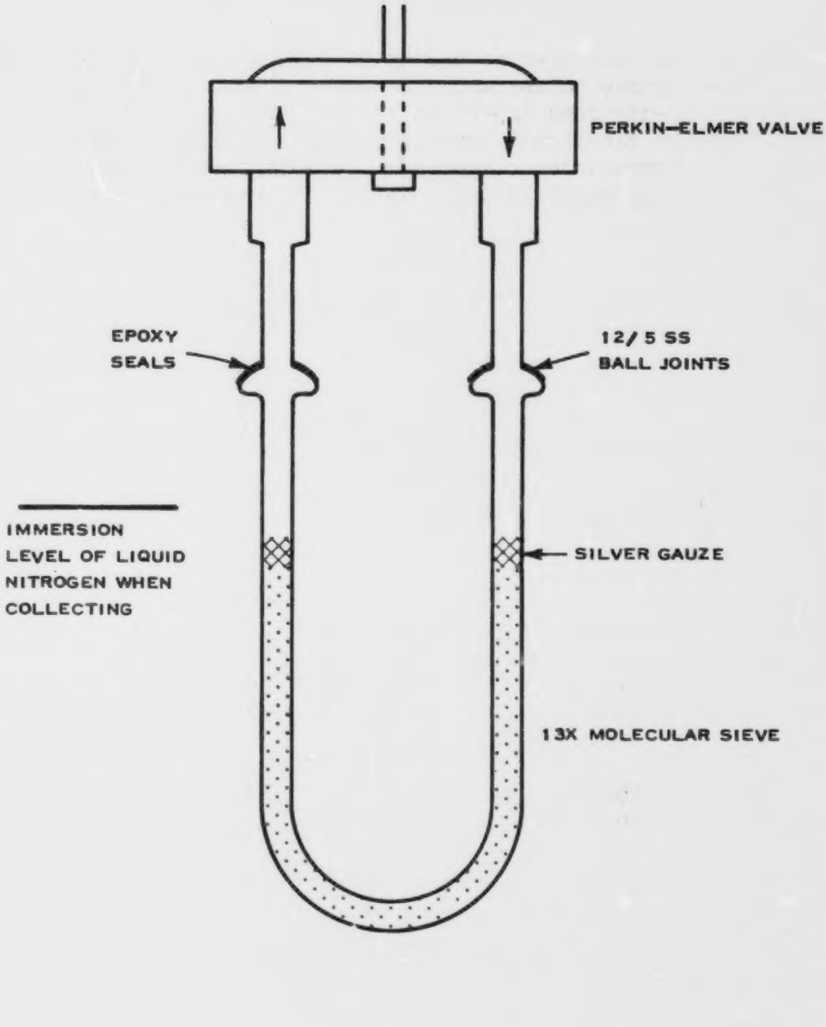
LEGEND

①	ROTAMETER
②	COMBUSTION TUBE
③	GAS BURNER
④	FURNACE, 900C
⑤	FURNACE, 550C, FOR U-TUBE
⑥	TRAP FOR CO_2, H_2O
⑦	PERKIN-ELMER VALVE
⑧	NITROGEN TRAP
⑨	THERMAL COND. DETECTOR
⑩	MOLE SIEVE COLUMN
⑪	BRIDGE, POWER SUPPLY
⑫	V. F. CONVERTER, COUNTER
⑬	STRIP RECORDER
⑭	SURGE TANK
⑮	SUB-ATM. CONTROL VALVE
⑯	PRESSURE REG., 6 PSIG
⑰	OUTLET PRESSURE MANOMETER
⑱	INLET PRESSURE MANOMETER
⑲	PRESSURE REG., 20 PSIG
⑳	PRESS. REG. VALVE, 30 PSIG
㉑	PURIFICATION TRAP
㉒	PURIFICATION TRAP

FIGURE 1
SCHEMATIC FLOW DIAGRAM

APPENDIX B

FIGURE 2
NITROGEN TRAP


PERKIN–ELMER VALVE
EPOXY SEALS
12/5 SS BALL JOINTS
IMMERSION LEVEL OF LIQUID NITROGEN WHEN COLLECTING
SILVER GAUZE
13X MOLECULAR SIEVE

APPENDIX C

PHILLIPS PETROLEUM COMPANY - METHOD 7304-AG*

MEASUREMENT OF HYDROCARBON GAS CHROMATOGRAPHIC (GLC) PROFILE OF CRUDE OILS AND THEIR RESIDUES

I. SCOPE

This procedure is for obtaining chromatograms of crude oils and crude oil residues for use in source identification studies.

II. OUTLINE OF METHOD

The sample (prepared according to Phillips Method 7128-AH-1) is placed in a glass sample holder and introduced into a vaporization chamber through a specially-designed injection system. The sample is flash vaporized and carried into the gas-liquid partition chromatography column with helium carrier gas. The hydrocarbon components are separated in the approximate order of their boiling points using temperature programmed gas chromatography.

III. APPARATUS

(a) Chromatograph. Any chromatograph which is equipped to take 1/4-in. diameter columns, has temperature-programming capability to 350°C, and is equipped with a flame ionization detector. A Perkin-Elmer Model 880 was used in the development of this method.

(b) Strip-Chart Recorder. 1-mv range and 2-second pen speed.

(c) Injection System. Designed by Phillips Petroleum Company. Includes injection system, vaporizer chamber, sample holder, and adapter and supports for installation on a Perkin-Elmer Model 880 gas chromatograph. The over-all sketch of this equipment is shown in Figure 1. Detailed drawings of this injection system are available from Phillips Petroleum Company under Drawing No. RS2-4053 (Note 1).

> NOTE 1: Basic design for above apparatus was adapted from Ramsdale, S. J., Wilkinson, R. E., J. Inst. Petroleum 54, No. 539, 326 (1968).

(d) Temperature Controller. Any controlling pyrometer which will control the temperature of the vaporizer chamber at 538°C ± 5°C.

IV. REAGENTS AND MATERIALS

(a) Helium.

(b) Hydrogen.

---

*Issued: January 17, 1973

(c) Cylinder Air.

(d) Chromosorb P. 40-60 Mesh, available from Johns Manville Company, Celite Division, New York, New York.

(e) Tubing. 1/4-inch O.D., stainless steel.

(f) Poly-m-Phenoxylene (PPE-20). Available from Varian Aerograph, Walnut Creek, California.

(g) Chloroform. Reagent Grade.

V. PRELIMINARY PREPARATIONS

(a) 5 Wt. % PPE-20 on Chromosorb P. Weigh 1 g of PPE-20 into a 100-ml beaker and add 80 ml of chloroform. Stir the mixture until completely dissolved and add the mixture to 19 g of Chromosorb P (40-60 mesh) in an 11-cm evaporating dish. Carefully evaporate the chloroform using low heat on a hot plate. Continue evaporation until the mixture appears dry.

(b) Column. Clean a 10-cm section of 1/4-inch O.D. stainless steel tubing and a 5-foot section of stainless steel tubing with a 100-volume wash of acetone and air-dry the tubing. Fill both lengths of tubing with the prepared packing (Section V,(a) and plug the ends of the tubing with glass wool. Connect the 10-cm pre-column section to the 5-foot analyzer section. Mount the column in the chromatograph so the pre-column section is at the inlet end.

(c) Column Conditioning. With the exit end of the column disconnected from the detector the column is conditioned as follows:

1. Establish a flow rate of 30 cc/min. of helium carrier gas through the column.
2. Program the column oven temperature from ambient to 300°C @ 6°/min. and hold at upper limit for two hours.
3. Increase column oven temperature to 380°C and maintain for 24 hours.
4. Cool column to ambient temperature and remove 5-foot analyzer section from pre-column section. Turn 5-foot section end for end and reconnect to pre-column and connect to detector and column is ready for use.

VI. PROCEDURE

Set the supply gases for optimum flame detector operation, the carrier gas flow at 30 cc/min. at ambient temperature, the controlling pyrometer to 538°C, the initial oven temperatures to 150°C and the temperature program rate control to 6°C/min. The instrument has equilibrated when the recorder baseline is stable.

Place the sample in the glass sample holder, using a small glass rod drawn to a medium point, by just dipping the tip of the rod in the sample and then rotating the tip around the inside wall of the sample holder (Note 2).

> NOTE 2: The viscosity of the sample determines the amount of sample clinging to the rod and repeatable sample sizes are difficult to achieve.

In Figure 1, open and close valves A and B in succession, allowing the sample to fall into the vaporization chamber without loss of sample vapors or carrier gas from the system. As soon as the sample holder drops into the vaporization chamber, initiate the temperature program controller and the separation of components over the temperature range of 150 to 350°C at a program rate of 6°/min. Record the chromatogram on the strip chart recorder. Retrieve the glass sample holder containing an enclosed iron core from the vaporization chamber with a magnet.

The pre-column section retains the high molecular weight material and should be changed after every 20 runs.

VII. DISCUSSION

Duplicate analyses, carried out several weeks apart, showed the method to be repeatable over extended periods of time.

The hydrocarbon GLC profiles for crude oil residues of known source are visually compared with samples of unknown source. Conclusions as to identity are based on the similarity or differences observed.

APPENDIX C

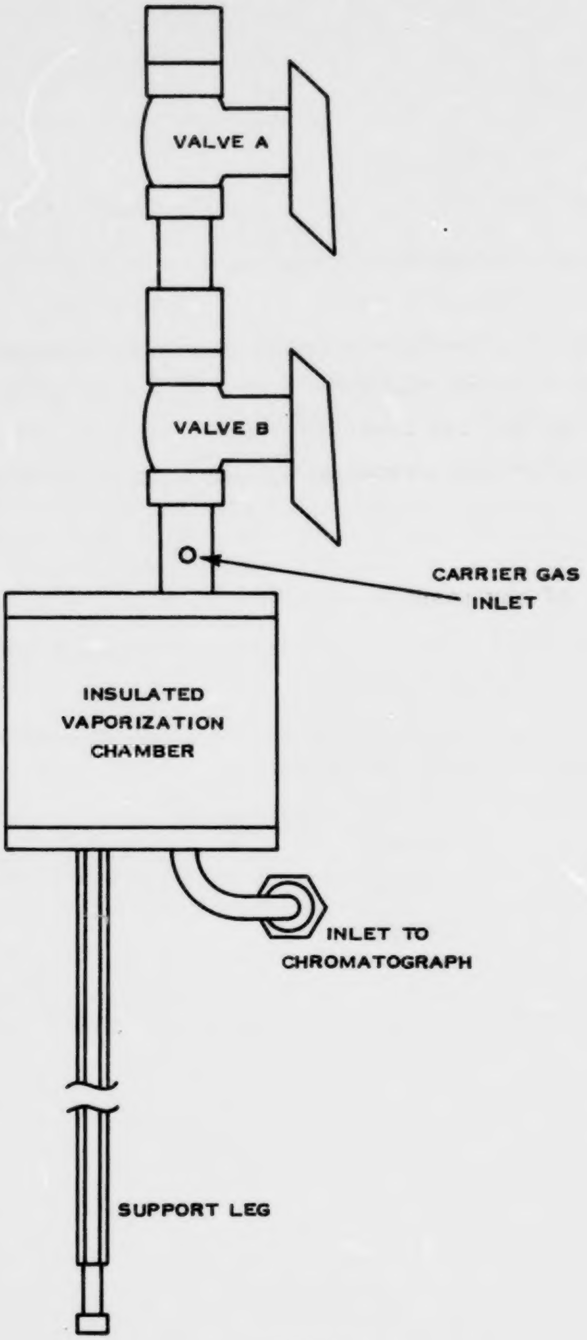

VALVE A
VALVE B
CARRIER GAS INLET
INSULATED VAPORIZATION CHAMBER
INLET TO CHROMATOGRAPH
SUPPORT LEG

FIGURE 1
INJECTION SYSTEM ADAPTED
FOR PERKIN–ELMER 880 CHROMATOGRAPH

APPENDIX D

ISOTOPE RATIO MASS SPECTROMETER INSTRUMENTATION

The isotope ratio mass spectrometer in this laboratory was built by Avco Corporation in Tulsa, Oklahoma. Two fundamental design characteristics make possible extremely precise isotope ratio measurements (1): (a) a sample inlet system that permits rapid, alternate introduction of sample gas and reference gas and (b) a dual collection system which permits electrical measurement of ratio signals from the simultaneous collection of major and minor isotopes. The mass analyzer is first order direction focusing with 35 cm radius of curvature, 90° angle of deflection and 12° beta axis focusing. The source and analyzer are evacuated with a 500 liter/second cold cathode sputter-ion pump which attains 10^{-9} torr in a clean system. The high voltage power supply is a Fluke Model 410B. The electromagnet is programmable from one to ten kilogauss and adjustable to within 0.5 gauss. The low voltage, high current-type magnet power supply is stable to one part in 100,000 for long term operation. The readout system includes dual vibrating reed electrometers and null ratio difference Kelvin Varley divider circuit, Cary Model 3125700, and a Sargent Model MR recorder.

Carbon isotope ratio measurements can be made precisely and conveniently by converting the carbon to carbon dioxide. One advantage of this is that carbon dioxide can be cleanly pumped out of the system in a short time so that "memory" effects are small. Phillips' geochemistry research program also requires isotope ratio measurements for sulfur, which is most conveniently run in the form of sulfur dioxide. Unfortunately, sulfur dioxide has a tendency to adhere to several substances which may exist within the mass spectrometer and inlet system and cause pumping difficulty. Furthermore, we have found that the initial instability of the output signal when sulfur dioxide is introduced to a clean mass spectrometer gradually improves with time. This indicates that the filament becomes "conditioned" in an atmosphere of sulfur dioxide.

Alterations were made in the sample handling region, outlined by dashed lines in Figure 1, so that carbon and sulfur isotope measurements can be readily made with the same mass spectrometer. The altered arrangement, shown in Figure 2, consists essentially of two separate identical inlet systems, one for carbon dioxide and the other for sulfur dioxide. When using the instrument to measure carbon isotope ratios, valves A and C are open and valves B and D are closed. Each system includes four single action solenoid valves, connected as shown, for alternately introducing sample and standard to the mass spectrometer. For each measurement, the sample is introduced into the spectrometer three times so that six measured differences between sample and standard are obtained. The δ values are calculated by using the average of these six instrumental measurements.

The precision for measuring carbon or sulfur isotope ratios is affected by sample preparation and reproducibility of the mass spectrometry measurement. Carbon dioxide suitable for mass spectrometry is prepared from organic carbon samples by a combustion method. Sulfur dioxide is prepared by pyrolysis of silver sulfide at 1000°C with copper oxide as the oxidant.

The over-all standard deviation for carbon isotope ratio determinations, calculated from results of 33 independent sample preparations and mass spectrometer measurements for a single laboratory working standard is 0.06. The standard deviation of instrumental error for carbon is 0.05, determined with 122 degrees of freedom by running the same carbon dioxide sample as both sample and standard.

APPENDIX D

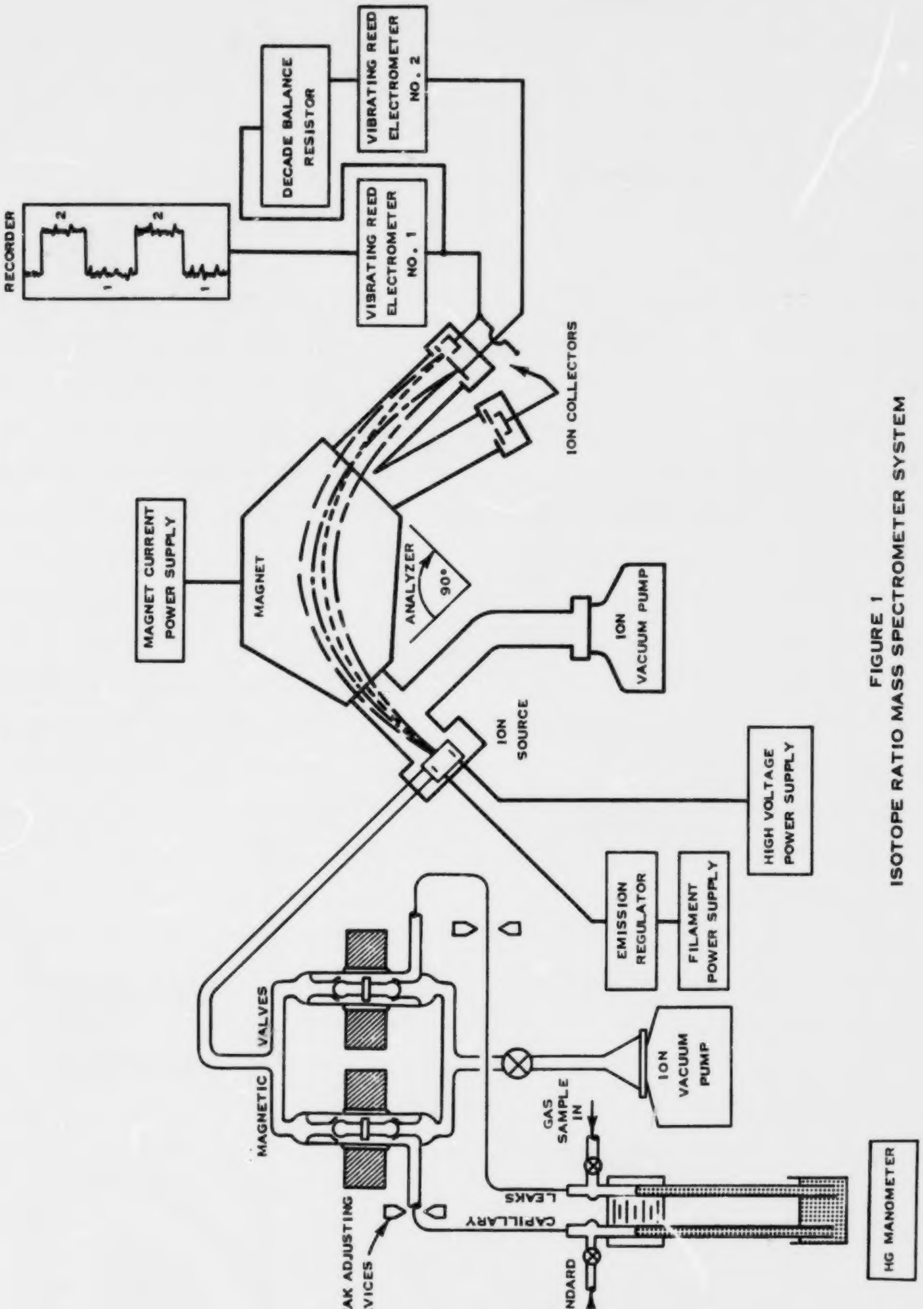

RECORDER
VIBRATING REED ELECTROMETER NO. 1
DECADE BALANCE RESISTOR
VIBRATING REED ELECTROMETER NO. 2
MAGNET CURRENT POWER SUPPLY
MAGNET
ANALYZER
90°
ION COLLECTORS
ION VACUUM PUMP
ION SOURCE
HIGH VOLTAGE POWER SUPPLY
EMISSION REGULATOR
FILAMENT POWER SUPPLY
MAGNETIC VALVES
ION VACUUM PUMP
LEAK ADJUSTING DEVICES
CAPILLARY LEAKS
GAS SAMPLE IN
GAS STANDARD IN
HG MANOMETER

FIGURE 1
ISOTOPE RATIO MASS SPECTROMETER SYSTEM

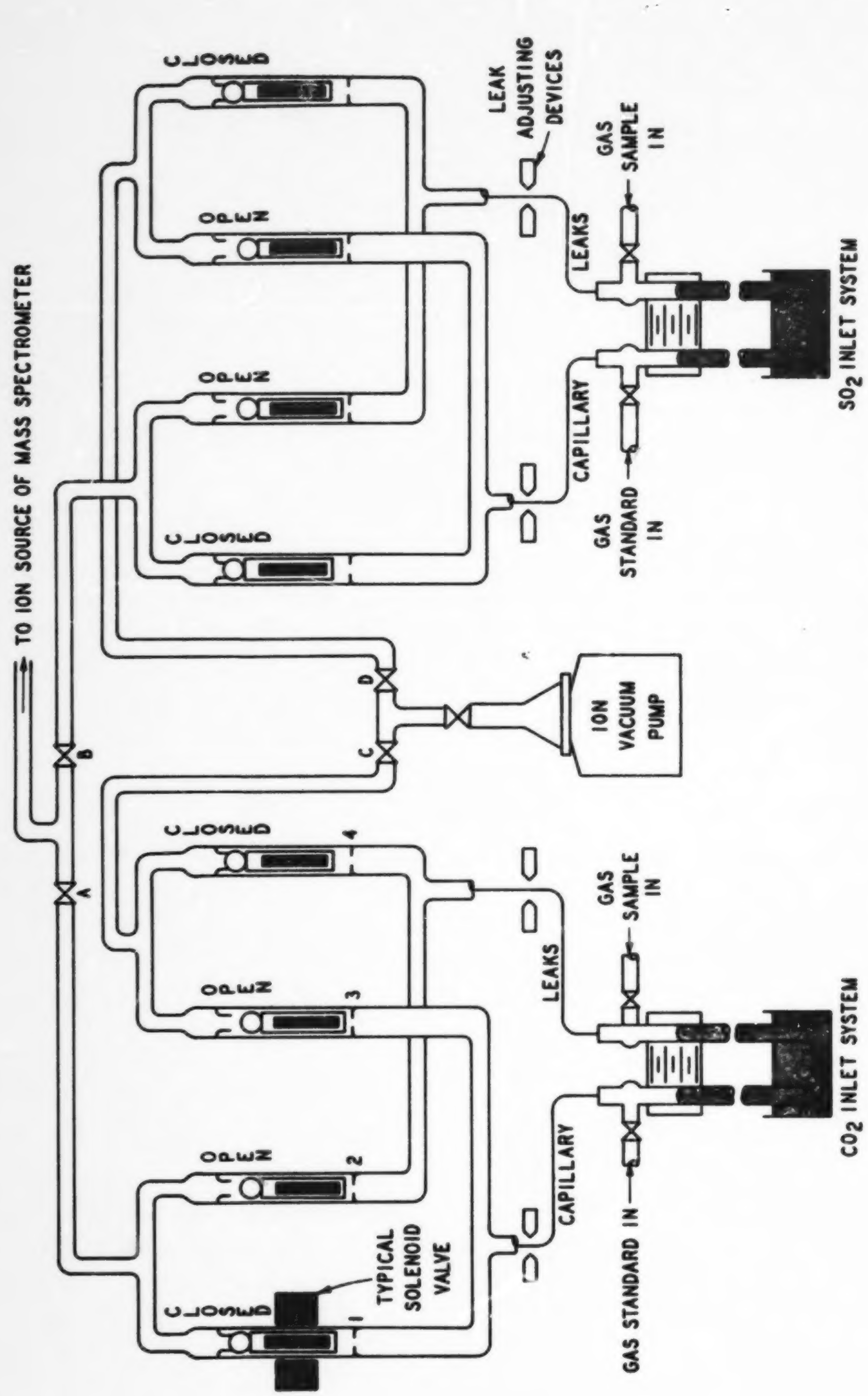

TO ION SOURCE OF MASS SPECTROMETER
A
B
C
D
ION VACUUM PUMP
CLOSED
OPEN
OPEN
CLOSED
CLOSED
OPEN
OPEN
CLOSED
1
2
3
4
TYPICAL SOLENOID VALVE
CAPILLARY
LEAKS
GAS STANDARD IN
GAS SAMPLE IN
CAPILLARY
LEAKS
GAS STANDARD IN
GAS SAMPLE IN
LEAK ADJUSTING DEVICES
CO_2 INLET SYSTEM
SO_2 INLET SYSTEM

FIGURE 2 - DUAL SAMPLE INLET SYSTEM

APPENDIX E

PHILLIPS PETROLEUM COMPANY - METHOD 7302-AF*

DETERMINATION OF TOTAL ORGANIC SULFUR IN OILS.

HYDROGENATION-GRAVIMETRIC SILVER SULFIDE METHOD.

I. SCOPE

This method is for the gravimetric determination of 0.5 to 10 per cent total organic sulfur in oils. The silver sulfide produced is suitable for use in isotope ratio mass spectrometric studies. Most inorganic sulfur including barium sulfate, if present, is measured also as organic sulfur.

II. OUTLINE OF METHOD

A weighed amount of oil is vaporized in an atmosphere of humidified hydrogen and passed over platinum gauze at 1100°C in a combustion tube. Organic sulfur is converted to hydrogen sulfide which is absorbed in a silver nitrate solution. The precipitated silver sulfide is filtered, washed, dried, and measured gravimetrically. The hydrogen ion concentration is titrated as an internal check of the results.

III. APPARATUS

(a) Hydrogenation (See Figure 1 for schematic diagram).

1. Flowmeter. For measuring hydrogen flow at 15 liters per hour, with a sensitivity to 2 per cent change in flow.
2. Combustion Tube. Fused silica, 20 mm I.D., 60 to 75 cm long, with 24/40 interjoint on the inlet and a reduced end at the exit.
3. Tube Furnace. 9 to 12 inches long and capable of maintaining a temperature of 1100 ± 10°C in its middle 3-inch section.
4. Pyrometer. Capable of indicating the temperature at 1100°C within ±10°C.
5. Combustion Boat. Platinum or porcelain, capable of holding 3 ml of sample.
6. Absorption Flask. 50-ml (see Figure 2).
7. Water Bubbler. (see Figure 1).
8. Analytical Balance.

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*Issued: January 10, 1973

(b) Gravimetric Measurements.

1. Crucibles. Gooch Type Low Form, medium porosity, fritted disc, 30-ml.

2. Drying Oven.

3. Filtering Flask. 500-ml.

(c) Titration.

1. pH Meter and Electrodes. Capable of determining end point of acid-base titration.

2. Magnetic Stirrer.

3. Buret.

IV. REAGENTS AND MATERIALS

All reagents are A.C.S. reagent grade or equivalent unless otherwise noted. References to water indicate distilled or deionized water.

(a) Hydrogenation.

1. Platinum Catalyst. Platinum-rhodium (90:10), 80-mesh gauze, 3 in. x 12 in.

2. Hydrogen. 99.5 per cent purity or better. It shall meet the requirement of Section V,(a) Hydrogenation, (1) c, d. A high-pressure cylinder shall be fitted with a pressure regulator to reduce the delivery pressure to 1 to 5 psi.

3. Sulfur Absorber. Activated charcoal packed absorption tube, approximately 3/4-in. (2-cm) diameter by 10 in. (25 cm) long with tubing connections on each end. (Note 1).

   NOTE 1: This item is not required if hydrogen purity permits absorbance specifications of Section V,(a) Hydrogenation, (1) d, to be met,

4. Silver Nitrate Solution, 0.1 N. Dissolve 16.99 g of silver nitrate in water and dilute to one liter.

5. Nitrogen. Prepurified grade or better.

(b) Gravimetric Measurements.

1. Ammonium Hydroxide, Concentrated.

(c) Titration.

1. Sodium Hydroxide, Standard 0.1 N. Standardized accurately against standard acid.

V. PROCEDURE

(a) Hydrogenation.

1. Preparation of Apparatus.

a. Wind the platinum-rhodium gauze into a tight roll 3 in. long and insert into the center of the refractory tube. Assemble all parts of the apparatus according to Figure 1 except the absorption flask, and connect with glass or aluminum tubing and a minimum of rubber or polyvinyl chloride tubing. Connect the hydrogen supply and fill the water bubbler about half full of distilled water.

b. Connect the outlet of the combustion tube to a vent line through which combustible gases can be discharged safely. Purge air from the system with nitrogen (Note 2) and start the flow of hydrogen. Adjust the hydrogen flow rate to 15 liters per hour and heat the furnace to 1100°C.

NOTE 2: Mixtures of hydrogen and air may explode in contact with platinum, even at ambient temperatures. Therefore, air must always be purged from the system with nitrogen or other inert gas before starting the hydrogen flow.

c. Place 30 ml of silver nitrate solution in a 50-ml absorption flask. Insert the stopper with bubbler tube. Disconnect the outlet of the refractory tube from the vent line and connect it to the inlet of the absorption flask. Connect the outlet of the absorption flask to the vent line. Continue passing hydrogen through the apparatus at a rate of 15 liters per hour for 50 minutes. Disconnect the absorption flask but continue the passage of hydrogen.

d. Determine the amount of silver sulfide produced according to Section V,(b) of this method. This blank should not exceed 1 mg.

e. Confirm satisfactory operation of the hydrogenation apparatus by analysis of an oil of known sulfur content using the procedures in Section V,(a), 2, of this method.

2. Analysis.

a. Weigh accurately 0.5 to 2.0 g of sample into a tared boat. (Note 3).

NOTE 3: Be careful that the amount of sample used does not produce more hydrogen sulfide than the silver nitrate solution can absorb. It may be necessary to make a preliminary analysis of the oil to determine the maximum amount of oil that can be used.

Insert the boat into the refractory tube. Prepare an absorption flask and connect it to the apparatus as in Section V,(a), (1), c. Purge the system for 5 minutes with nitrogen.

b. With the hydrogen flowing at 15 liters per hour, heat the sample by passing current through nichrome resistance wire wrapped around the combustion tube in the region of the boat. The sample should be heated and volatilized at such a rate that carbon is not formed at the outlet end of the refractory tube. Some samples may require 8 hours for volatilization.

c. At the finish, some carbonaceous residues may remain in the boat. Using a Meker burner at maximum heat, heat the combustion tube in the area of the boat and in the area between the boat and the furnace to red heat. Continue the hydrogen sweep for 20 minutes. Purge hydrogen from the system with nitrogen and remove the absorption flask from the train. Pass air through the refractory tube for 5 minutes to remove any carbon collected on the platinum gauze. Purge the system again with nitrogen before starting hydrogen flow for the next run (Note 4).

NOTE 4: To prevent an explosion due to slight valve leakage, the air and hydrogen supplies must not be connected to the system at the same time. Physically disconnect and separate one supply from the system before connecting the other.

d. Save the silver nitrate solution in the absorption flask for the gravimetric measurements and titration.

(b) Gravimetric Measurements.

1. Preparation of Apparatus.

a. Wash filtering crucible with water, ammonium hydroxide and water using vacuum filtration. Dry in vacuum oven at 60°C for 2 hours.

b. Cool to room temperature in a desiccator. Determine tare weight.

2. Filtering, Washing and Drying of Silver Sulfide.

a. Filter the silver nitrate solution from Section V,(a), 2 through the tared filtering crucible. With the aid of a policeman, quantitatively transfer the silver sulfide into the crucible. Save the filtrate in the filtering flask for titration, Section V,(a), 2.

b. Use another filtering flask to collect the three 10-ml water, two 10-ml concentrated ammonium hydroxide solution, and three 10-ml water washings of the silver sulfide. Discard the washings. Dry the crucible in a vacuum oven at 60°C for 2 hours and cool to room temperature in a desiccator. Determine the gross weight.

(c) Titration.

1. Titration of Filtrate.

a. Transfer filtrate into beaker and titrate with 0.1 N standardized sodium hydroxide, using a pH meter to determine the maximum inflection point (approximately 5.5 pH).

b. Record the volume of sodium hydroxide used.

VI. CALCULATIONS

(a) Gravimetric Measurements.

$$\text{Sulfur, weight per cent} = \frac{A\ 12.94}{g}$$

where: A = grams silver sulfide
g = grams of sample

(b) Titration.

$$\text{Sulfur, weight per cent} = \frac{BN\ 1.603}{g}$$

where: B = ml of NaOH solution used
N = normality of NaOH solution
g = grams of sample

VII. PRECISION

For crude oils containing 1-4 per cent sulfur, the following precision data were obtained:

Method	Standard Deviation	Degrees of Freedom	Repeatability
Gravimetric	0.0464%	16	0.14%
Titration	0.109%	16	0.33%
ASTM D1552*	0.0914%	10	0.29%

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*ASTM D1552: "Standard Method of Test for Sulfur in Petroleum Products (High Temperature Method)", 1972 ASTM Standards, Part 18.

APPENDIX E

PHILLIPS PETROLEUM COMPANY – METHOD 7302–AF

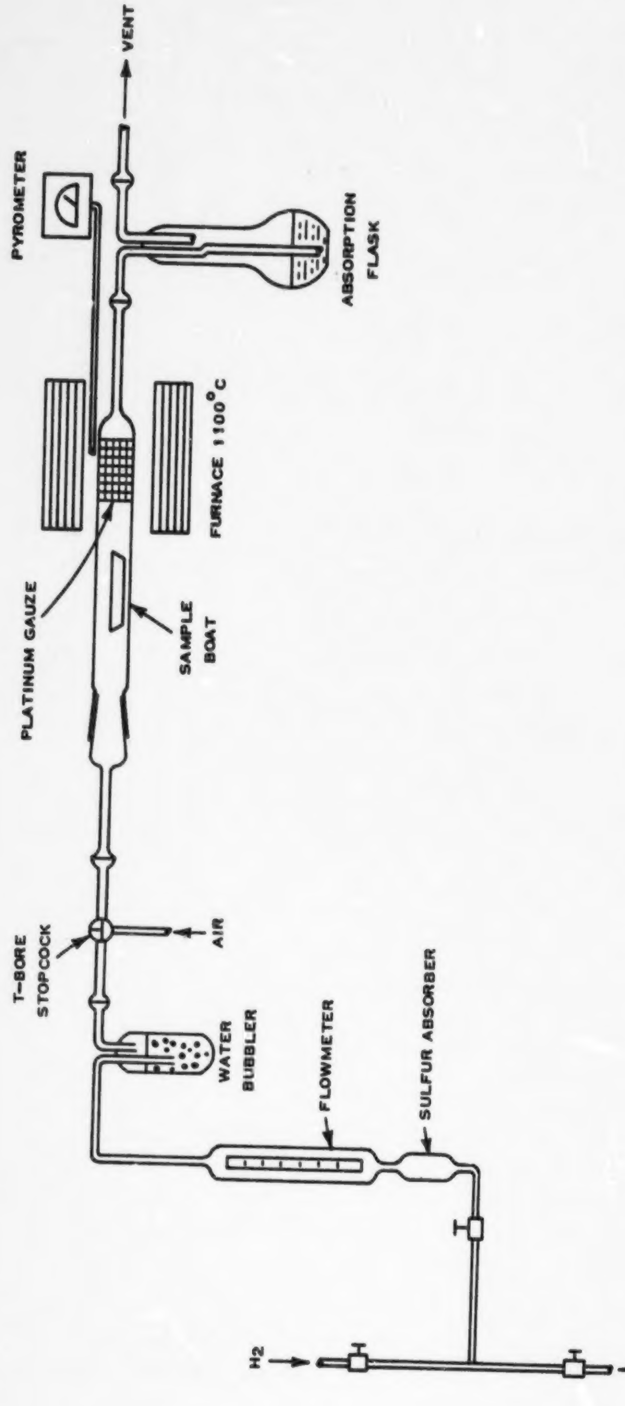
H2
N2
SULFUR ABSORBER
FLOWMETER
WATER BUBBLER
T–BORE STOPCOCK
AIR
PLATINUM GAUZE
SAMPLE BOAT
FURNACE 1100°C
PYROMETER
ABSORPTION FLASK
VENT

FIGURE 1
SCHEMATIC DIAGRAM OF HYDROGENATION APPARATUS

APPENDIX E

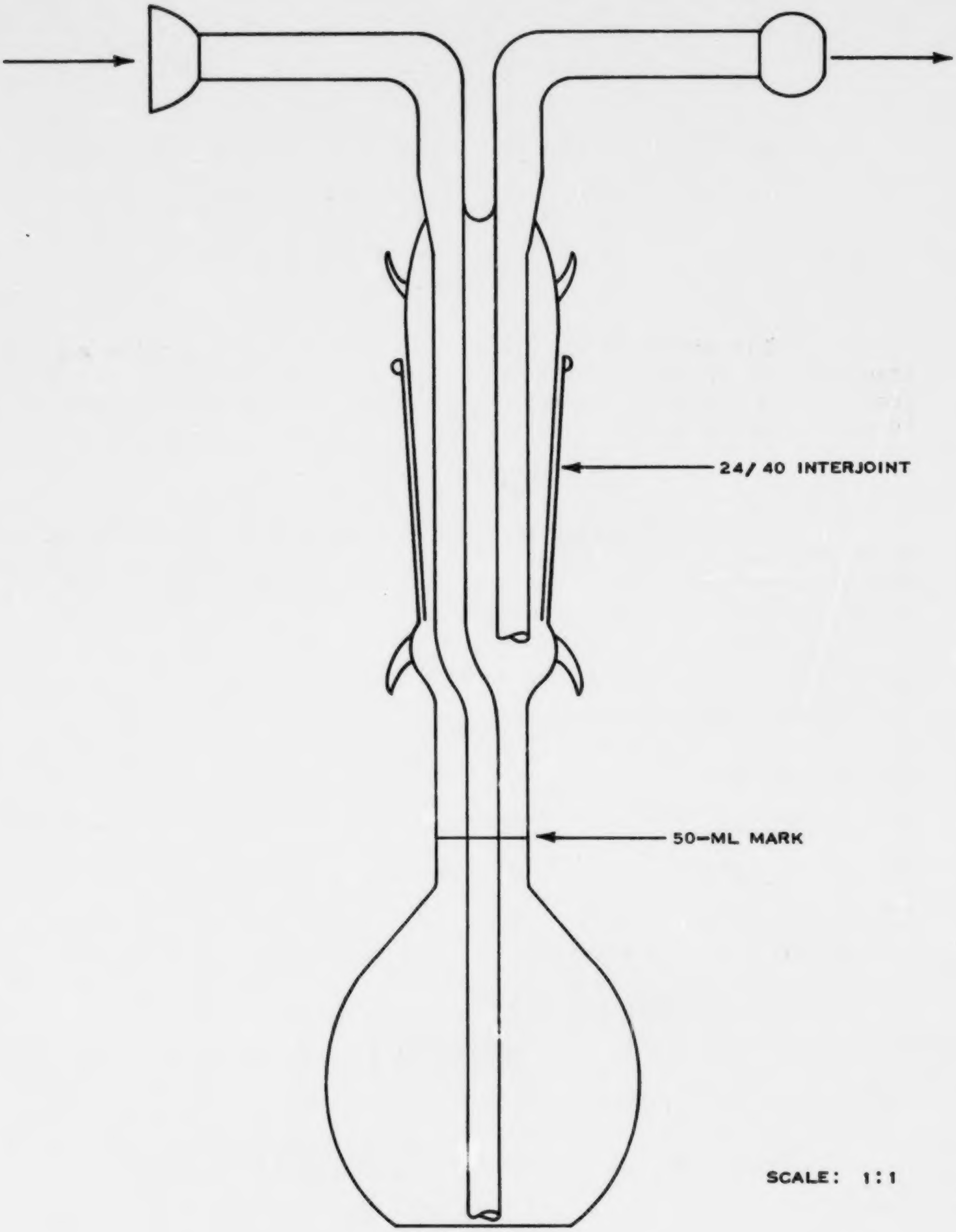
24/40 INTERJOINT
50-ML MARK
SCALE: 1:1

FIGURE 2
50-ML ABSORPTION FLASK

APPENDIX F

PHILLIPS PETROLEUM COMPANY - METHOD 7303-AZ

PREPARATION OF SULFUR DIOXIDE GAS FROM SILVER SULFIDE SAMPLES FOR ISOTOPE RATIO MASS SPECTROMETRY

I. SCOPE

This method is for the preparation of sulfur dioxide gas, without fractionation of the sulfur isotopes, from samples of silver sulfide prepared from various sources. The gas must be pure in order for the mass spectrometer to operate properly.

II. OUTLINE OF METHOD

A sample of silver sulfide is mixed with copper oxide and roasted in an evacuated quartz tube at 1050°C. The sulfur dioxide is purified, measured and transferred to an evacuated glass sample bomb for measurement on the isotope ratio mass spectrometer.

III. APPARATUS

(a) Vacuum Line-Combustion Apparatus. Figure 1.

(b) Tube Furnace. Capable of maintaining temperature of 1050 ± 20°C.

(c) Pyrometer. Capable of measuring the temperature at 1050°C within ±20°C.

(d) Sample Tube. Fused silica, 9 mm O.D., sealed at one end, 5 cm long.

(e) Magnetic Sample Carrier. Fused silica tube with Alnico V magnet sealed in one end. Opening on other end large enough to accept sample tube.

(f) Analytical Balance.

(g) Dewar Flask. Pyrex, 1 quart (2 required).

(h) Dewar Flask. Pyrex, 1/2-pint (4 required).

(i) Glass Sample Bulbs. 25 cc.

IV. REAGENTS AND MATERIALS

(a) Cupric Oxide. Powder, ACS Reagent Grade.

(b) Copper Metal Turnings. Washed with acetone and dried before use.

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[*] Issued: January 12, 1973

(c) Toluene Slush Bath, -95°C. Cool toluene in a dewar flask by careful addition of liquid nitrogen until a liquid-solid slurry of even consistency is formed. Stir while cooling.

(d) Pentane Slush Bath, -130°C. Cool n-pentane in same manner as described above.

(e) Liquid Nitrogen.

V. PROCEDURE

(a) Preparation of Vacuum System. Turn on all pumps, gauges and utilities. Evacuate the entire system to a pressure of 1 x 10^{-5} torr or less. Fill dewar flask around the trap nearest to the diffusion pump with liquid nitrogen. Adjust furnace so that a temperature of 1050°C is maintained inside central portion of combustion tube.

(b) Sample Preparation. Obtain tare weight of sample tube using an analytical balance. Carefully weigh 30-40 mg of finely divided Ag_2S and 120-160 mg CuO powder into the tube. Mix the two powders by carefully rotating and shaking the tube. Place small plug of copper turnings in open end of sample tube.

(c) Introduction of Sample into Vacuum System.

1. Close stopcock 2.
2. Open stopcock 3.
3. Remove end cap.
4. Place sample tube in magnetic sample carrier. (If sample tube is too loose, quartz wool may be inserted to secure tube.)
5. Place carrier with sample in cool portion of combustion tube.
6. Replace end cap.

(d) Evacuation of Combustion Tube Using Rough Vacuum.

7. Close stopcocks 1 and 4.
8. Open stopcock 5.
9. Close stopcock 3.
10. Open stopcock 2, wait 1-2 minutes.

(e) Evacuation of Combustion Tube Using Hard Vacuum.

11. Close stopcock 5.

12. Open stopcock 4. Wait until vacuum of 1×10^{-5} torr or better is attained.

(f) Preparation of Sulfur Dioxide.

13. Place dewar flask containing liquid nitrogen on trap 1.

14. Slowly slide sample into hot zone using an external magnet.

    Pressure on thermocouple gauge will rise to a maximum of about 100 microns then drop back to zero. After pressure drops (O_2 production ceases) wait approximately 5 minutes.

15. Slowly slide sample holder into cool zone.

16. Close stopcock 2.

(g) Purification of Sulfur Dioxide. Part I. Removal of less volatile impurities such as H_2O, SO_3, etc.

17. Place dewar flask containing liquid nitrogen on trap 2. Remove liquid nitrogen from trap 1. Allow transfer of gases to continue until trap 1 reaches room temperature.

18. Close stopcocks 4 and 7.

19. Remove liquid nitrogen from trap 2 and place toluene slush bath on trap 2 immediately. (Check to make sure slush bath is of proper consistency.)

20. Close stopcocks 8 and 9.

21. Open stopcock 7.

22. Place dewar containing liquid nitrogen on cold finger (trap 3). Allow transfer to continue for 3 minutes.

23. Close stopcock 11.

24. Warm cold finger (trap 3) to room temperature. Read pressure on manometer.

(h) Purification of Sulfur Dioxide. Part II. Reomval of more volatile impurities such as CO_2, etc.

25. Place dewar flask containing liquid nitrogen on cold finger (trap 3).

26. Remove liquid nitrogen and place pentane slush on cold finger.

27. Open stopcocks 8 and 11.

28. Monitor pressure on ion gauge. After initial pressure increase, pressure will slowly decrease to near its former level.

29. Close stopcock 11.

30. Remove pentane slush bath and allow cold finger to warm to room temperature. Measure pressure of SO_2 using mercury manometer.

(i) Transfer of Sulfur Dioxide to Glass Sample Bomb.

31. Open stopcocks 8, 9 and 10. Evacuate system to pressure of 1×10^{-5} torr or less.

32. Close stopcock 8.

33. Cool glass sample bulb with dewar flask containing liquid nitrogen.

34. Open stopcock 11. Allow SO_2 to be frozen in glass sample bomb.

35. Open stopcock 8. Wait until pressure is 1×10^{-5} torr or less.

36. Close stopcocks 9 and 10. Detach glass sample bulb from vacuum system and store for isotope ratio mass spectrometry.

37. Prepare system for preparation of next sample.

(j) Preparation of System for Next Sample.

38. Close stopcock 8.

39. Remove slush bath from trap 2.

40. Open stopcocks 6 and 7.

41. Place new sample bulb in place and open stopcock 9.

42. Open stopcock 10. Wait 2 minutes for system to pump down.

43. Close stopcock 6.

44. Open stopcocks 8 and 4.

45. Return to procedure (b) for continuation.

VI. CALCULATIONS

Data recorded includes:

1. Wt. Ag_2S used.
2. Wt. CuO used.
3. Pressure SO_2 + more volatile materials.
4. Pressure SO_2.

The per cent yield of SO_2 is calculated. The Theoretical yield of SO_2 (pressure in mm) is calculated from the known weight of silver sulfide (Note 1).

$$\text{Yield } SO_2, \% = \frac{\text{pressure } SO_2 \text{ (mm)}}{\text{theoretical pressure (mm)}} \times 100$$

NOTE 1: The calculation of theoretical pressure of SO_2 is lengthy and will only be summarized. The volume of the cold finger and manometer can be measured using standard techniques. The volume will depend on the pressure of the system and will have an equation of the form $V = V_o + aP$. Assuming that SO_2 behaves as an ideal gas at the pressures encountered, the pressure of SO_2 gas expected from a given weight of Ag_2S can be calculated. Since these calculations involve the solution of a second degree equation, it is easiest to utilize a computer to generate a table of theoretical pressures of SO_2 vs. weight of Ag_2S. Such a table has been generated and should be used in the above calculation. CAUTION: If the appropriate weight of Ag_2S is not in the table or if the volume of the appropriate portion of the vacuum line has been changed since the calibration was made, consult technical supervisor before proceeding.

VII. PRECISION

An evaluation of the data from 82 consecutive conversions of different Ag_2S samples showed:

Maximum yield - 101%
Minimum yield - 79%
Average yield - 93.5%
Standard Deviation - 4.48

SO_2 samples obtained in less than 90 per cent yield should be considered suspect.

APPENDIX F

PHILLIPS PETROLEUM COMPANY - METHOD 7303-AZ

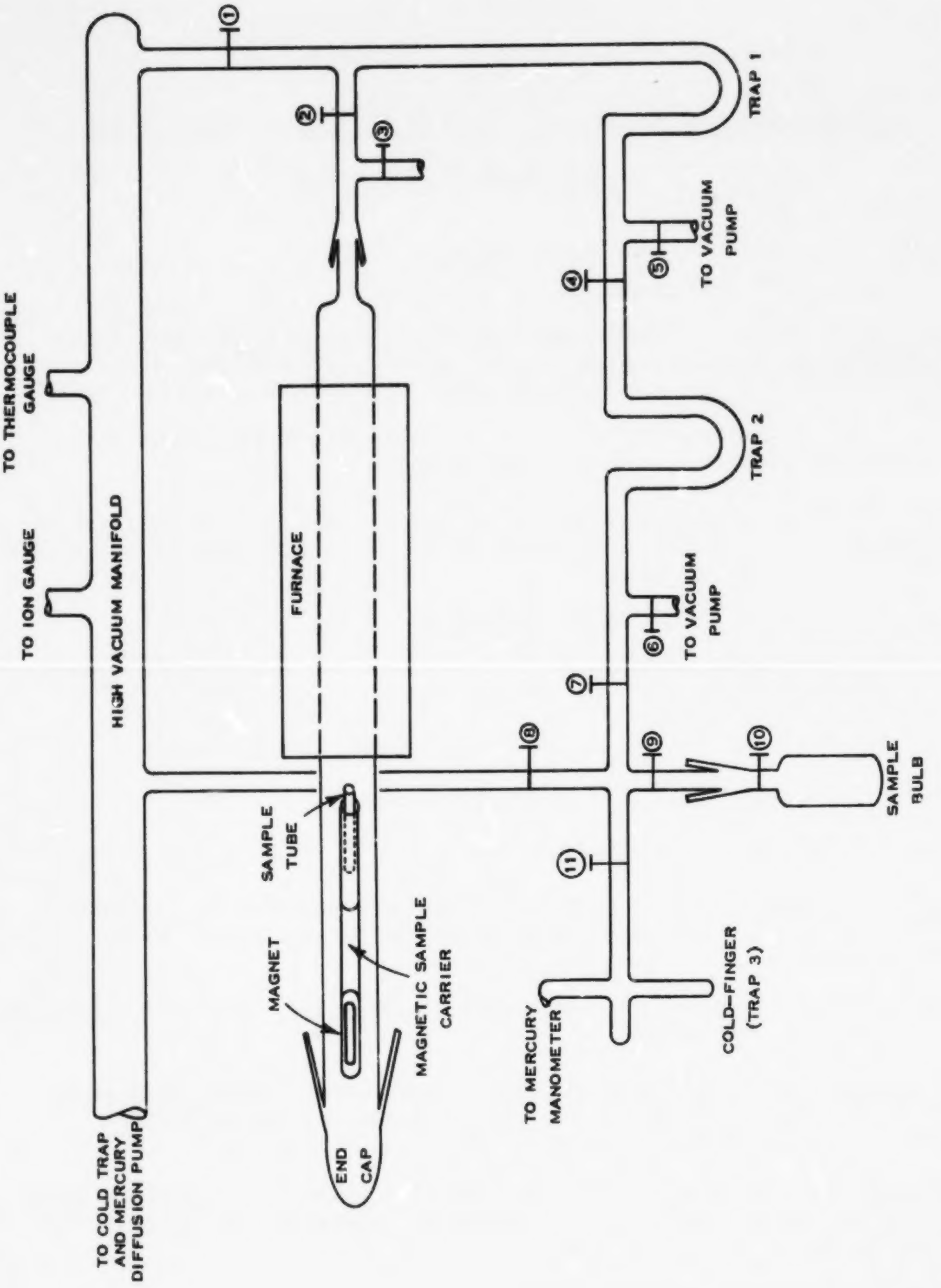
TO ION GAUGE
TO THERMOCOUPLE GAUGE
HIGH VACUUM MANIFOLD
TO COLD TRAP AND MERCURY DIFFUSION PUMP
①
②
③
FURNACE
SAMPLE TUBE
MAGNET
MAGNETIC SAMPLE CARRIER
END CAP
TRAP 1
④
⑤
TO VACUUM PUMP
TRAP 2
⑥
TO VACUUM PUMP
⑦
⑧
⑨
⑩
SAMPLE BULB
⑪
TO MERCURY MANOMETER
COLD-FINGER (TRAP 3)

FIGURE 1
VACUUM LINE--COMBUSTION APPARATUS

APPENDIX G

PHILLIPS PETROLEUM COMPANY - METHOD 6511-AF-1*

OXYGEN FLASK COMBUSTION - GRAVIMETRIC METHOD FOR DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS

I. SCOPE

This method is for the determination of 5 to 50 per cent total sulfur in organic compounds which can be burned in a Schöniger oxygen combustion flask. It is applicable to solid samples and to liquids of low volatility.

II. OUTLINE OF METHOD

A 25- to 50-milligram sample is ignited in a combustion flask containing oxygen. The sulfur, as sulfate in the flask washings, is determined gravimetrically as barium sulfate.

III. APPARATUS

(a) Analytical Balance. Accurate to ±0.1 mg.

(b) Filtering Crucibles. 30-ml, porous porcelain, fine porosity.

(c) Muffle Furnace. Capable of operating at 800 C.

(d) Oven. Electric, operated at 110 C.

(e) Sample Wrappers. Filter paper cut to a shape and size to facilitate wrapping, folding and igniting samples. Arthur H. Thomas Co. No. 6471-F or equivalent.

(f) Schöniger Combustion Unit. With electric ignition. Arthur H. Thomas Co. No. 6471-H or equivalent.

(g) Schöniger Combustion Flask. 1000-ml, borosilicate glass, with glass hooks and 29/29 interjoint. Arthur H. Thomas Co. No. 6471-H10 or equivalent. (Also available in 500-ml and 2000-ml sizes.)

(h) Stopper for Combustion Flask. Borosilicate glass, with platinum gauze basket and electrical contact. Arthur H. Thomas Co. No. 6471-H15 or equivalent.

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*Issued: April 1, 1965 as VO-65R
Revised: December 21, 1972

IV. REAGENTS AND MATERIALS

All reagents are ACS reagent grade unless otherwise noted. References to water indicate distilled or deionized water.

(a) Barium Chloride Solution. Dissolve 100 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 1 liter.

(b) Hydrogen Peroxide. 30 per cent solution.

(c) Hydrochloric Acid. Concentrated, sp. gr. 1.18.

(d) Oxygen. Commercial grade cylinder oxygen is satisfactory.

(e) Sodium Carbonate Solution. 2 per cent aqueous.

V. PROCEDURE

(a) Combustion. Weigh 25 to 50 mg (to nearest 0.1 mg) on a paper sample wrapper. Fold the paper and attach it to the platinum cradle of the flask stopper. Add 10 ml of 2 per cent sodium carbonate solution to the combustion flask. Purge the flask with oxygen from an oxygen cylinder for 20 to 30 seconds. Moisten the glass stopper with water and immediately insert the stopper and sample into the flask. Attach the flask to the ignition unit and turn the plastic shield end for end to place the flask behind the shield in an inverted position. Press the firing button to ignite the sample.

After combustion is complete, remove the flask from the ignition unit. Shake the flask at intervals and let stand (or cool in ice) until vapor absorption is complete. Remove the stopper from the flask and rinse with water, catching the rinsings in the flask. Quantitatively transfer the contents of the flask to a 600-ml beaker. Wash the combustion flask quantitatively and add the rinsings to the beaker. Add water to attain a volume of 250-300 ml.

(b) Determination of Sulfur. Add 2 ml of concentrated HCl and 2 drops of 30 per cent hydrogen peroxide to the beaker and evaporate to approximately 200 ml on a hot plate. Adjust the heat to maintain slow boiling of the solution and add 10 ml of barium chloride solution, either in a fine stream or dropwise. Stir the solution during the addition and for 2 minutes thereafter. Cover the beaker with a fluted cover glass and continue boiling slowly until the solution has evaporated to a volume of approximately 75 ml. Remove the beaker from the hot plate and allow to cool for at least 1 hour before filtering.

Filter the supernatant liquid through a tared ($\pm$0.1 mg) fine-porosity porcelain filtering crucible. Wash the barium sulfate precipitate with water, first by decantation and then in the crucible, until free of chloride. Dry the crucible and contents in an oven at 110 C for 1 hour, and ignite in a muffle furnace at 800 C for 1 hour. Allow the crucible to cool to room temperature in a desiccator, and weigh to ±0.1 mg.

VI. CALCULATIONS

Calculate the sulfur content of the sample as follows:

$$\text{Sulfur, wt. \%} = \frac{13.73\ B}{W}$$

where: B = grams of $BaSO_4$ precipitate
W = grams of sample

VII. PRECISION

Statistical evaluation of data from duplicate analyses on 94 samples by three different analysts showed:

Range, Wt. % S	Degrees of Freedom	Standard Deviation	Repeatability
5 to 10	22	0.132%	0.39%
10 to 20	41	0.153	0.44
20 to 50	31	0.296	0.86

Duplicate determinations should be considered suspect if they differ by more than the repeatability shown (95 per cent confidence level).

REFERENCES

1. Schöniger, W., Mikrochim, Acta., (1956), 869.

2. Lysyj, I. and Zarembo, J. E., Anal. Chem. 30, 428 (1958).

3. Martin, A. J. and Deveraux, H., Anal. Chem. 31, 1932 (1959).

APPENDIX H

PHILLIPS PETROLEUM COMPANY - METHOD 7301-AZ*

PREPARATION OF SILVER SULFIDE FROM BARIUM SULFATE

HYDRIODIC ACID REDUCTION METHOD

I. SCOPE

This method is for the preparation, without fractionation of the sulfur isotopes, of silver sulfide from barium sulfate. The silver sulfide produced is suitable for use in isotope ratio mass spectrometric studies.

II. OUTLINE OF METHOD

A weighed sample of barium sulfate is added to a solution containing hydriodic acid, hypophosphorous acid and hydrochloric acid. The hydrogen sulfide produced is washed with water and absorbed in a cadmium acetate solution. The cadmium sulfide produced is converted to silver sulfide and determined gravimetrically.

III. APPARATUS

(a) Flask. Boiling, 250 ml, round-bottomed, with gas inlet tube.

(b) Condenser.

(c) Vacuum Trap. Plain, 6 in., 2 needed.

(d) Centrifuge Tube. 100-ml.

(e) Analytical Balance.

(f) Heating Mantle.

(g) Pasteur Pipette. Disposable.

IV. REAGENTS AND MATERIALS

All reagents are ACS reagent grade unless otherwise noted. References to water indicate distilled or deionized water.

(a) Reducing Solution. Mix 500 ml (850 g) hydriodic acid (d = 1.7), 816 ml hydrochloric acid, concentrated, and 245 ml hypophosphorous acid, H_3PO_2 (50 per cent) in a large Erlenmeyer flask. Boil solution for 45 minutes to remove any sulfur present by expelling as H_2S (use hood). (Note 1)

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*Issued: January 10, 1973

NOTE 1: An alternate reducing solution giving equally satisfactory results is made by mixing 567 g sodium iodide, 245 g sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$, and 180 ml water. Heat mixture until a clear solution is obtained, then add 1310 ml hydrochloric acid, concentrated. Stir for 10 minutes, cool to room temperature, and filter mixture. Discard precipitate. Boil solution for 45 minutes to remove any sulfur present.

(b) Cadmium Acetate Solution, 0.1 N. Dissolve 26.65 g $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ in water and dilute to one liter.

(c) Silver Nitrate Solution, 0.1 N. Dissolve 16.99 g of $AgNO_3$ in water and dilute to one liter.

(d) Nitrogen. Prepurified grade or better.

V. PROCEDURE

(a) Preparation of Apparatus.

1. Assemble apparatus as shown in Figure 1. Mount trap 1 in reverse manner as shown, fill trap 2 with distilled water.

2. Add 100 ml of reducing solution and several boiling beads. Adjust nitrogen to give moderate flow and heat solution to boiling. Boil 30 minutes. Add cadmium acetate solution to centrifuge tube and continue boiling for 15 minutes. If no yellow precipitate is formed in the cadmium acetate solution, the system is ready for use. If yellow precipitate forms, continue boiling until all sulfur has been expelled as evidenced by lack of yellow precipitate formation when fresh cadmium acetate is placed in centrifuge tube. Cool reducing solution to room temperature.

(b) Barium Sulfate Reduction.

1. Carefully weigh 25-200 mg $BaSO_4$ into a small boat. Wash $BaSO_4$ into flask containing reducing solution using 1-10 ml distilled water.

2. Adjust nitrogen flow, make certain centrifuge tube contains about 75 ml of colorless cadmium acetate solution. Boil solution for about 4 hours or until all of the sulfur has been collected as cadmium sulfide. Add acetone to cadmium acetate to reduce foaming if necessary.

(c) Conversion to Silver Sulfide.

1. Fill centrifuge tube to 100 ml mark with water. Centrifuge for 5-10 minutes. Decant supernatant liquid. Add 50 ml distilled water and mix thoroughly. Add 50 ml silver nitrate solution, mix thoroughly and let stand 1 hour.

2. Wash filtering crucible with water, ammonium hydroxide and water using vacuum filtration. Dry in vacuum oven at 60°C for 2 hours. Cool to room temperature and determine tare weight.

3. Filter silver nitrate-silver sulfide mixture through the tared filtering crucible. Wash precipitate with ammonium hydroxide and water. Dry in vacuum oven at 60°C for 2 hours. Cool to room temperature and determine weight of silver sulfide.

4. Save silver sulfide if needed for further studies. Wash filtering crucible with chromic acid to clean.

VI. CALCULATIONS

(a) Theoretical Yield

$$\text{weight } Ag_2S \text{ (theoretical)} = \text{weight } BaSO_4 \times 1.062$$

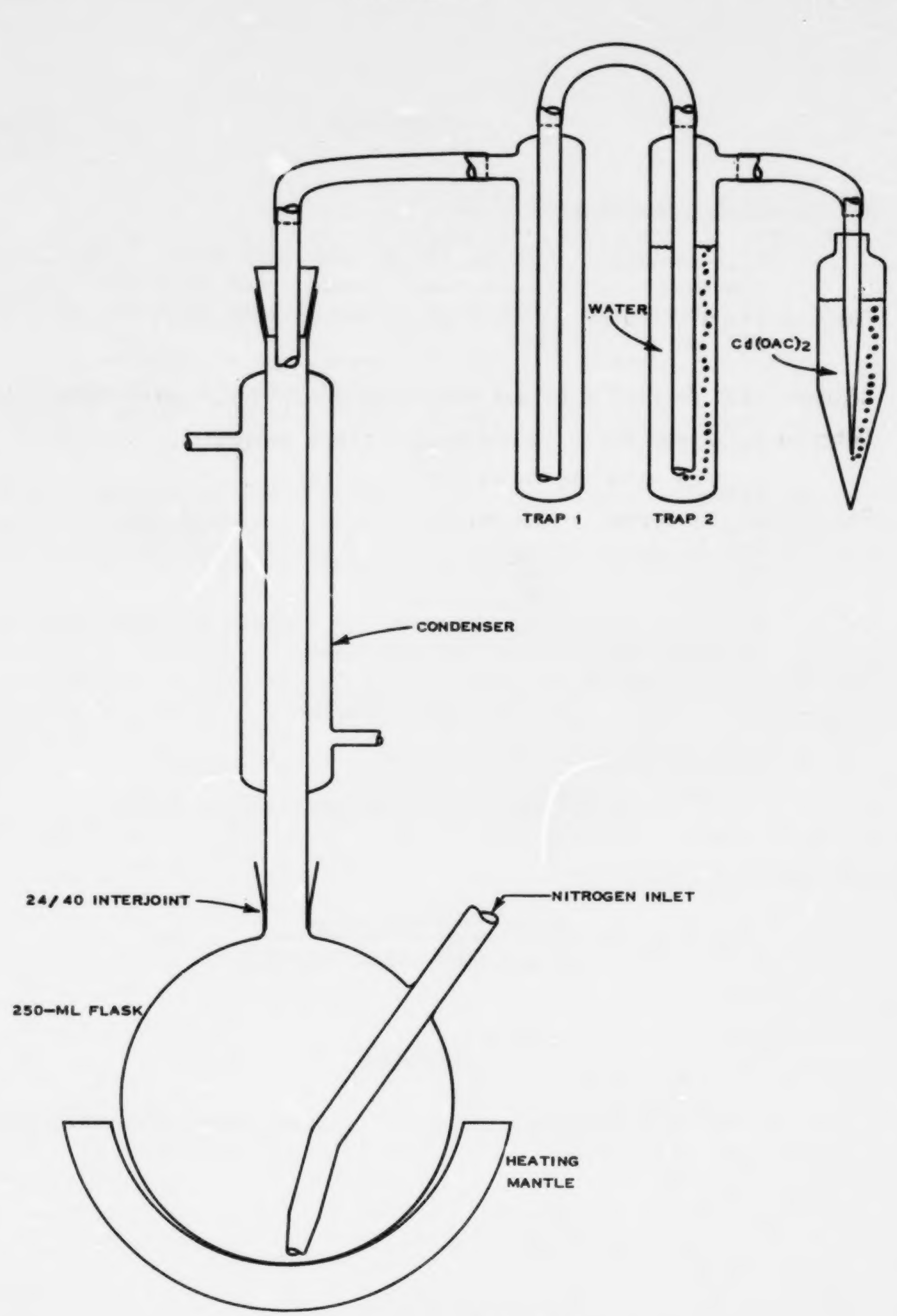
(b) Per Cent Yield

$$\text{Yield (\%)} = \frac{\text{weight } Ag_2S \text{ recovered}}{\text{weight } Ag_2S \text{ (theoretical)}} \times 100$$

REFERENCE

1. H. G. Thode, J. Monster, and H. B. Dunford, Geochimica et Cosmochimica Acta, 25, 159 (1961).

APPENDIX H


WATER
Cd(OAC)2
TRAP 1
TRAP 2
CONDENSER
24/40 INTERJOINT
NITROGEN INLET
250-ML FLASK
HEATING
MANTLE

PHILLIPS PETROLEUM COMPANY - METHOD 7301-AZ

FIGURE 1
APPARATUS FOR $BaSO_4$ REDUCTION

APPENDIX I

OPERATING CONDITIONS FOR SULFUR GLC PROFILE MEASUREMENT

Chromatograph: Tracor 550 with glass injection system. Flame photometric detector mounted on heated block.

Column: 100 feet x 0.01 inch Stainless Steel coated with Dexsil 300.

Detector: Tracor Model 100 AT Melpar flame photometric detector used with 394 nm sulfur-selective filter.

Gas Flows: Hydrogen 150 ml/min
Oxygen 20 ml/min
Air 100 ml/min

Carrier Gas: Helium at 30 psig to give column flow of 7 ml/min.

Column Temperature: 100°C initial, programmed at 5°C/min to 330°C and held for 16 minutes at 330°C.

Injection point: 350°C

Column outlet: 330°C

Detector base: 330°C

Chart speed: 1 inch per minute

Sample size: 2 microliters of a 9 weight percent solution of 600+F bottoms in cyclohexane

Cooling period: 16 minutes

Equilibration period: 16 minutes

APPENDIX J

PHILLIPS PETROLEUM COMPANY - METHOD 7204-AZ*

SILICA GEL SEPARATION OF 600$^+$F BOTTOMS FROM CRUDE OIL

I. SCOPE

This method is for the separation of 600$^+$F bottoms from crude oil into saturate, aromatic, and asphaltic fractions by silica gel liquid-solid elution chromatography.

II. OUTLINE OF METHOD

A sample of 600$^+$F bottoms in crude oil is placed on a silica gel column. The column is eluted successively with n-pentane, dichloromethane, and a methyl alcohol-dichloromethane mixture. The column effluents from each solvent are collected and the solvent removed by evaporation to recover the three fractions. The amount of each fraction recovered is weighed and the per cent distribution of the bottoms among the saturate, aromatic, and asphaltic fractions is calculated.

III. APPARATUS

(a) Balance. Analytical, 5 place.

(b) Chromatographic Column and Solvent Reservoir, Figure 1. The chromatographic system is assembled from components available from Fischer & Porter Co., Lab-Crest Division, County Line Road, Warminster, Pa., 18974. Catalog numbers are designated where applicable.

1. Chromatographic column with threaded glass and Teflon needle valve and Teflon drip tip, 1/2" I.D. x 24" length. Catalog No. 274-472.
2. Glass coupling, aluminum, glass-to-glass, 1/2" I.D. Catalog No. 687-004-0012.
3. Strip neoprene asbestos for use with couplings. Catalog No. 688-366-0012.
4. Interface gasket for threaded metal coupling for 1/2" I.D. pipe, Teflon machined envelope with silicone rubber filler. Catalog No. 691-006.
5. Solvent reservoir, 300 ml capacity, graduated, with glass pipe, 1/2" I.D., exit and 28/15 female ball joint on inlet. Use glass pipe joint, Catalog No. 670-000-1206, 1/2" I.D. x 6" length, to fabricate the solvent reservoir as shown in Figure 1.

(c) Bottles. 2 oz., wide mouth.

(d) Vials. 2 dram.

(e) Roto-Vac Evaporator. Sargent-Welch Scientific Co., Dallas, Texas. Catalog No. S-31211.

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*Issued: March 8, 1972

(f) Flask. 500 ml, 24/40, round-bottom.

(g) Soxhlet Extraction Apparatus. Fisher Scientific Co., Pittsburgh, Pa. Catalog No. 9-556C. I.D. of glass extraction tube - 50 mm.

(h) Syringe and Needle. 2 cc, 6 inch needle.

(i) Water Bath. Organomation Assoc. N-Evap Model 10, Worchester, Mass., is satisfactory.

(j) Funnel. Buchner type, Coors, Porcelain. O.D. 67 mm, plate diameter 56 mm. Fisher Scientific Co., Pittsburgh, Pa. Catalog No. 10-356B.

(k) Flask. Filtering, graduated, with Side Tube, 500 ml. Fisher Scientific Co. Catalog No. 10-181E.

IV. REAGENTS AND MATERIALS

(a) Methyl Alcohol. Merck and Co., Inc., Rahway, N.J.

(b) n-Pentane. (Distilled in glass) Use as received from Burdick and Jackson Laboratories, Inc., Muskegon, Michigan.

(c) Dichloromethane. Distilled. Add 25 g of calcium sulfate to 4 kg of Eastman Kodak dichloromethane to remove water. Mix thoroughly. Filter through Whatman 40 filter paper and distill. Discard the first 100 ml of distillate. Collect the remaining distillate and store it in bottles having Teflon-lined caps. The following distillation apparatus is satisfactory.

1. Distillation column-vacuum jacketed with an integral liquid fraction take off, ground ball seat and vertical coil condenser. One meter length, 2 cm I.D., packed with pyrex Helix rings.
2. Distillation kettle - 3 liter.
3. Reflux ratio - 1 volume reflux to 5 volumes take off.

(d) Silica Gel. Activated, W. R. Grace Co., Grade 923, 100-200 mesh. Curtin Scientific Co., Box 1546, Houston, Texas 77001.

Purify the silica gel before use as follows: Using the Soxhlet extraction apparatus fill the glass extraction tube with silica gel, assemble the apparatus, and fill the flask about half-full of methyl alcohol. Extract the silica gel for a minimum of 8 hours. Remove the extraction tube containing the alcohol-wet silica gel from the apparatus. Insert the extraction tube in a small Buchner funnel, which is mounted on a filter flask and attached to a vacuum source. Make a vacuum-tight seal between the wall of the extraction tube and the wall of the Buchner funnel with a short length of rubber tubing. Apply vacuum to the flask until the methyl alcohol ceases to flow from the extractor tube. Pour the silica gel from the extractor tube into an evaporating dish. Complete the removal of the methyl alcohol by placing the evaporating dish on a hot plate. Mix the warm silica gel occasionally until a free-flowing powder is obtained. Activate the silica gel at 800°F (427°C) overnight. Store the activated material in a bottle having a Teflon-lined screw cap.

(e) Nitrogen Regulator and Cylinder.

(f) Glass Wool.

V. PROCEDURE

(a) Column Preparation. Assemble the column and reservoir as shown in Figure 1. Place a small piece of glass wool at the bottom of the column. Rinse the column and reservoir with dichloromethane. Discard the washings. Rinse the column and reservoir with n-pentane and discard the washings. Add 100 ml of n-pentane to the column with the stopcock closed. Add 60 ml of silica gel to the column and shake in order to make a slurry of silica gel in n-pentane. Allow the silica gel to settle and proceed to Section V (b) during this period.

(b) Sample Transfer and Saturate Fraction. Into a tared 2 dram vial add about 0.25 g of the 600°F bottoms sample and weigh. Add 2 ml of n-pentane to the vial to dissolve the sample. Transfer the resulting solution to the top of the column by means of a needle and syringe. Repeat both the addition of n-pentane to the vial and the transfer of the solution to the column until the sample is completely transferred to the top of the silica gel column. In many cases the sample is not completely soluble in n-pentane and an insoluble residue remains in the vial. Save this residue for Section V (c). Apply 5 psig nitrogen pressure to the top of the solvent reservoir. Open the stopcock and collect the n-pentane in a clean, dry 500 ml round-bottom flask until the n-pentane level is 1 inch above the top of the silica gel. Do not let the silica gel go dry. The flow rate of all the solvents is about 10 ml per minute.

Add 200 ml of n-pentane to the solvent reservoir. Apply 5 psig nitrogen pressure. Continue to collect the column effluent in the 500 ml flask until the n-pentane level is 1 inch above the top of the silica gel. Proceed to Section V (c) to obtain the aromatic fraction.

Place the flask on the rotary-vacuum evaporator and remove the solvent completely at about 60°C and sufficient vacuum to gently boil the solvent. The saturates fraction is normally colorless and careful technique is required to insure quantitative transfer of this fraction to the vial. (The aromatic and asphaltic fractions are dark-colored and the completeness of quantitative transfer can be observed visually.) Transfer quantitatively the saturates fraction from the round-bottom flask to a tared vial using dichloromethane as solvent which is added in small increments (1-2 ml) and allowed to flow down the walls of the flask. Transfer each solvent increment to the vial by needle and syringe before adding the next solvent increment. A total of 9 ml of dichloromethane is sufficient for quantitative transfer without exceeding the capacity of the vial. Place the vial in the water bath at 50-60°C and turn on the nitrogen flow to evaporate the solvent. Cool, dry and weigh the vial. The increase in weight of the vial over the tare weight represents the saturate fraction, S grams. Store the vial containing the saturate fraction in a capped 2 oz. wide-mouth bottle.

(c) Aromatic Fraction. Some samples are not completely soluble in n-pentane and the sample vial will contain the insoluble residue from Section V (b). Add a few ml of dichloromethane to the vial to dissolve the residue. Transfer the resulting solution to the top of the column by means of a needle and syringe. Repeat the dichloromethane addition and transfer twice to completely transfer the sample to the column.

For the majority of the 600$^+$F bottoms the sample will be completely soluble at this point. If any insoluble residue remains, place the sample vial in the water bath to remove the solvent. Cool, dry, and weigh the vial. Any increase in weight over the tare weight represents sample that was not transferred to the column. The maximum amount of material recoverable from the column is the original sample weight, W grams, less the insoluble residue, R grams.

Add 200 ml of dichloromethane to the solvent reservoir. Apply 5 psig nitrogen pressure. Collect the effluent in a clean, dry 500 ml round-bottom flask until the dichloromethane level is 1 inch above the top of the silica gel column. Do not let the silica gel go dry. Proceed to Section V (d) to obtain the asphaltic fraction.

Place the flask on the rotary-vacuum evaporator and remove the solvents completely. Transfer quantitatively the aromatic fraction from the round-bottom flask to a tared vial using dichloromethane as solvent. Place the vial in the water bath and turn on the nitrogen flow to evaporate the solvent. Cool, dry and weigh the vial. The increase in weight of the vial over the tare weight represents the aromatic fraction, A grams. Store the vial containing the aromatic fraction in a capped 2 oz. wide-mouth bottle.

(d) Asphaltic Fraction. Add 200 ml of mixed solvent (75 vol. % methyl alcohol/25 vol. % dichloromethane) to the solvent reservoir. Apply 5 psig nitrogen pressure. Collect the effluent in a clean, dry 500 ml round-bottom flask until all the solvent has drained from the column. (Allow the column to run dry.) Place the flask on the rotary-vacuum evaporator and remove the solvents. Transfer quantitatively the asphaltic fraction from the round-bottom flask to a tared vial using dichloromethane as solvent. Place the vial in the water bath and turn on the nitrogen flow to evaporate the solvent. Cool, dry and weigh the vial. The increase in weight of the vial over the tare weight represents the asphaltic fraction, C grams.

(e) Silica Gel Removal. Silica gel may be removed from the column as follows: With the reservoir top open to the air and the stopcock open, pull a vacuum on the column for 2 hours. The dry silica can then be poured out of the column into a sealable can for appropriate disposal.

VI. CALCULATIONS

(a) Distribution, Normalized.

1. Saturates, weight per cent = $\frac{S\ 100}{S + A + C}$

2. Aromatics, weight per cent = $\frac{A\ 100}{S + A + C}$

3. Asphaltics, weight per cent = $\frac{C\ 100}{S + A + C}$

(b) Recovery.

Silica gel recovery, weight per cent = $\frac{(S + A + C)\ 100}{(W - R)}$

where: S = grams in saturate fraction

A = grams in aromatic fraction

C = grams in asphaltic fraction

W = grams 600^{+}F bottoms weighed into the sample vial

R = grams insoluble residue not transferred to the column

APPENDIX J

PHILLIPS PETROLEUM COMPANY - METHOD 7204-AZ

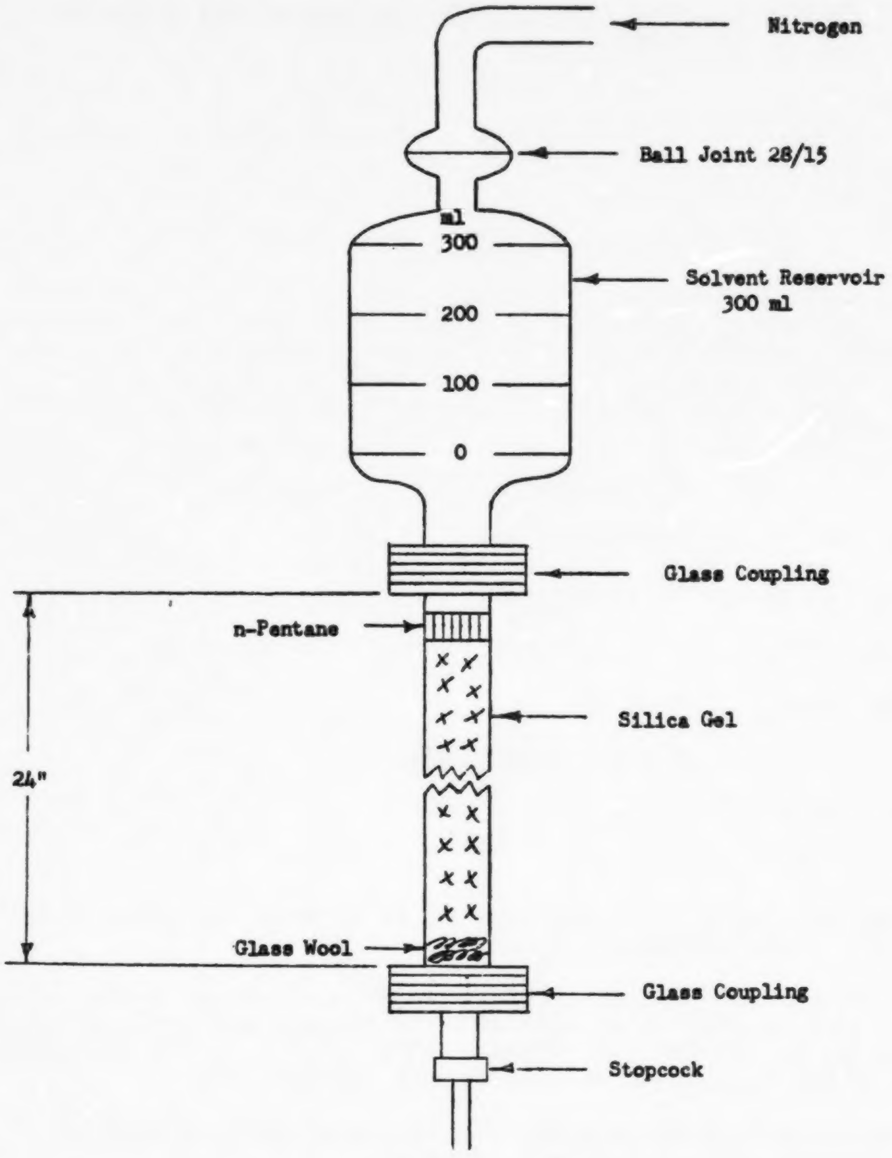
Nitrogen
Ball Joint 28/15
ml
300
200
100
0
Solvent Reservoir 300 ml
Glass Coupling
n-Pentane
Silica Gel
24"
Glass Wool
Glass Coupling
Stopcock

FIGURE 1. CHROMATOGRAPHIC COLUMN AND SOLVENT RESERVOIR

APPENDIX K

PHILLIPS PETROLEUM COMPANY - METHOD 7214-AZ*

ISOLATION OF n-PARAFFINS FROM SATURATE FRACTIONS BY UREA ADDUCTION

I. SCOPE

This method is for the preparation of a urea adduct to isolate the n-paraffins from the saturate fraction obtained by silica gel separation of 600$^+$F bottoms of crude oil.

II. OUTLINE OF METHOD

A sample of the saturate fraction is dissolved in a benzene-methyl alcohol mixture. Methyl alcohol saturated with urea is mixed with the sample. The urea adduct precipitate which forms is allowed to stand overnight. Solvent is removed and the urea adduct is dried. The carbon-number distribution is measured by gas-liquid chromatography of the isolated n-paraffins (Phillips Method 7215-AG).

III. APPARATUS

(a) Vials. Two-dram, Teflon-lined caps.

(b) Syringe and Needle. 5-cc, 23-gauge.

(c) Spatula. Micro.

(d) Pipets. Pasteur, disposable.

IV. REAGENTS AND MATERIALS

(a) Methyl Alcohol. Reagent Grade.

(b) Benzene. Reagent Grade.

(c) Benzene-Methyl Alcohol Solvent. Add 300 ml of benzene to 100 ml of methyl alcohol and mix thoroughly.

(d) Urea. Recrystallize as follows: Saturate 200 ml of methyl alcohol with urea. Heat the solution to about 50 C and add more urea until saturated. Decant the hot solution into a beaker, allow to cool to room temperature. Pour off the solution and collect the recrystallized urea.

(e) Saturated Urea in Methyl Alcohol. Add recrystallized urea to 50 ml of methyl alcohol to form a saturated solution.

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*Issued: May 25, 1972

V. PROCEDURE

Transfer about 50 mg of saturate fraction obtained from the silica gel separation (Phillips Method 7204-AZ) into a clean dry 2-dram vial with the aid of a micro spatula or a disposable pipet. Add 5 ml of benzene-methyl alcohol solvent and cap the vial. Shake until the sample dissolves. Add 2 ml of saturated urea in methyl alcohol solution and mix thoroughly. A precipitate comprised of urea and the urea adduct of the n-paraffins is formed. Allow the precipitate to stand overnight. Remove the solvent from the vial by using a syringe with a 23 gauge needle. The inside diameter of the needle is small enough to prevent removal of precipitate. Allow the precipitate to dry by leaving the cap off the vial for several hours. Recap the vial containing the dry urea adduct and save for gas-liquid chromatography.

APPENDIX L

PHILLIPS PETROLEUM COMPANY - METHOD 7305-AG*

DETERMINATION OF RELATIVE WEIGHT DISTRIBUTION OF n-PARAFFINS UREA ADDUCTED FROM CRUDE OIL FRACTIONS, C_{13} TO C_{38} BOILING RANGE

I. SCOPE

This method determines the relative weight distribution of n-paraffins adducted from crude oils and their fractions in the boiling range of C_{13} to C_{38} n-paraffins.

II. OUTLINE OF METHOD

The adduct sample (prepared according to Method 7214-AZ) is dissolved in water to reduce the n-paraffins which are extracted into cyclohexane solvent for analysis. Using n-C_{40} as an internal reference time standard (the cyclohexane solvent contains $\sim$0.25 weight per cent n-C_{40}) the n-paraffins are separated on a gas-liquid partition chromatography column. The output signal from the flame ionization detector is sent directly to a central computer processor where data acquisition and reduction programs provide a weight per cent distribution of n-paraffins, a mol per cent distribution of n-paraffins, smoothed weight per cent data, CEP values (a weight ratio of odd-carbon-numbered to even-carbon-numbered members of a homologous series), and graphical plots of all the above data except mol per cent distribution.

III. APPARATUS

(a) Chromatograph. Any chromatograph which is equipped to take 1/8-inch diameter columns, has temperature programming capability to 380°C, and is equipped with a flame ionization detector. A Perkin-Elmer Model 880 gas chromatograph was used in the development of this method.

(b) Strip-Chart Recorder. 1-mv range and 2-second pen speed or faster.

(c) Microliter Syringe. Model #1705, gas-tight, available from Hamilton Company, Inc., Whittier, California.

(d) Automatic Data Acquisition and Reduction System. A minimum of an electronic integrator to determine the areas of the n-paraffin peaks reduces analysis time of this method from 2.5 hours to 40 minutes. This procedure uses an IBM 1800 computer for on-line data acquisition and reduction. A typical computer output from this procedure is attached to this method as Appendix I (Note 1).

NOTE 1: Except for the weight per cent report appearing on pages 1 and 2 of Appendix I, all subsequent data in Appendix I is generated from these data. The computer programs for this data reduction are included in Core Load Link Program Number 7.

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*Issued: January 18, 1973

IV. REAGENTS AND MATERIALS

(a) Helium.

(b) Hydrogen.

(c) Cylinder Air.

(d) Chromosorb P. 80-100 Mesh, available from Johns Manville Company, Celite Division, New York, New York.

(e) Tubing. 1/8-inch O.D., stainless steel.

(f) Poly-m-Phenoxylene (PPE 20). Available from Varian Aerograph, Walnut Creek, California.

(g) Chloroform. Reagent Grade.

(h) Cyclohexane. Research Grade, available from Phillips Petroleum Company, Special Products Division, Bartlesville, Oklahoma.

(i) n-Tetracontane (C-40). Available from Poly Science Corporation, Chemical Division, Evanston, Illinois.

V. PRELIMINARY PREPARATIONS

(a) 16.7 Weight Per Cent PPE 20) on Chromosorb P. Weigh 6 g of PPE 20 into a 250 ml beaker and add 150 ml of chloroform. Stir the mixture until completely dissolved and add the mixture to 30 g of 80-100 mesh Chromosorb P in a 15-cm evaporating dish. Carefully evaporate, while stirring, the chloroform using low heat on a hot plate. Continue evaporation until the mixture appears dry.

(b) Column. Clean a 10-foot length of 1/8-inch O.D. stainless steel tubing with a 100 volume wash of benzene followed by a 50 volume wash of acetone and air dry the tubing. Fill the tubing with the prepared packing (Section V,a) by bending the tubing into a U shape and filling each side of the U, vibrating the tubing gently during filling. Plug the ends of the column with glass wool and shape the column so it can be conveniently mounted in the chromatograph.

(c) Column Conditioning. With the exit end of the column disconnected from the detector, condition the column as follows:

1. Establish a helium carrier gas flow of 22 cc/min. through the column at ambient temperature.

2. Program the column oven temperature from ambient to 300°C @ 6°/min. and hold at upper limit for two hours.

3. Increase column oven temperature to 380°C and maintain for three hours.

4. Cool oven to 320°C amd maintain column at this temperature for twelve hours.

5. Cool oven to ambient temperature, disconnect column from inlet and reconnect so that exit end of column during conditioning period is now connected to inlet side of chromatograph. Connect column to the detector and column is ready for use.

VI. PROCEDURE

Set the detector supply gases for optimum flame detector operation, the carrier gas flow to 22 cc/min. at ambient temperature, the upper limit of temperature programming to 370°, the initial column oven temperature to 150°C, and the temperature program rate control to 12°c/min. The instrument has equilibrated when the recorder baseline is stable.

Place the available urea-n-paraffin adduct in a 2-dram vial and dissolve in approximately 5 ml of hot distilled water to release the adducted hydrocarbon. Using the following table, add the indicated amount of cyclohexane containing 0.25 weight per cent n-C_{40} (Note 2).

NOTE 2: The n-C_{40} is an internal reference time standard only for updating retention time changes in the computer job definition. Relative sensitivity values for the flame ionization detector are assumed to be unity for all the n-paraffins measured by this method.

Mg Adduct	Cyclohexane Solvent
1	1 drop
10	5 drops
20	10 drops

Cap the vial and agitate gently by tapping twice.

Inject 2 microliters of the cyclohexane phase into the chromatograph for all adduct samples of 10 mg or more. Inject a maximum of 5 ul into the chromatograph for the smallest adduct samples. Immediately after sample injection, initiate the temperature programmer and the computer data acquisition control switches. Record the chromatogram on the strip chart recorder. A typical chromatogram of a C_{13} to C_{38} adduct sample is shown in Figure 1.

VII. CALCULATIONS

If hand calculations are required to obtain the relative weight distribution of the n-paraffins in the adduct samples, peak areas of the individual n-paraffin peaks are measured by peak height times the width of the peak at 1/2 the peak height. Calculate the weight per cent distribution of n-paraffins as follows:

$$C_i, \text{ Wt. } \% = \frac{i\ (100)}{\sum S_i}$$

where: C_i = concentration of ith component, weight per cent
i = area of ith component
$\sum S_i$ = sum of areas of all ith components in sample

VIII. PRECISION

A statistical evaluation of 12 sets of duplicate analyses showed the following:

Range, Wt. %	Degrees of Freedom	Standard Deviation	Repeatability
0 - 1.0	69	0.06253	0.1769
1.0 - 10.0	210	0.2657	0.7440

APPENDIX L

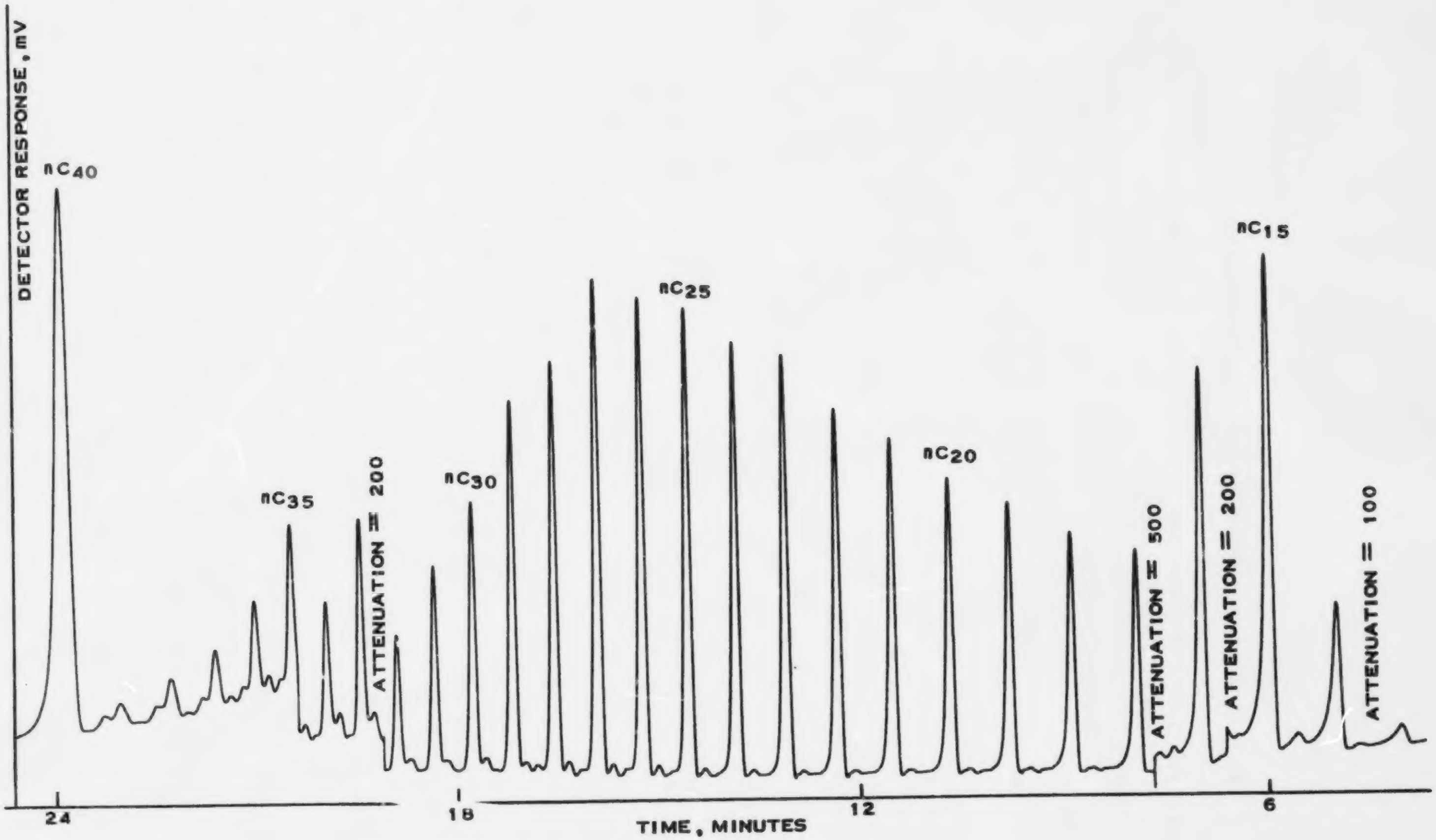

FIGURE 1
TYPICAL n-PARAFFIN GAS CHROMATOGRAM

APPENDIX L

PHILLIPS PETROLEUM COMPANY - METHOD 7305-AG

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                                  APPENDIX I
                  PHILLIPS PETROLEUM COMPANY - R&D DEPARTMENT
                        AUTOMATED INSTRUMENT ANALYSIS

DATE= 4/ 4/72  11.30  TITLE= C13-C38 ADDUCTS-GEOCHEM                     JOB NO.  226

INSTRUMENT NO.   16   ANALYST= COJ   FEATURE NO. 6094   RUN NO.  1 OF  1   CALC NO. 904

SAMPLE ID= 1-61F    HJ-20246-1-61F   GLC# 721366
                          EPA #61
SAMPLE RUN=  4/ 4/72   11.03         ANALYST C.D. Jackson..............DATE 4-4-72......

  EXPECTED ACTUAL  RATIO  DELTA
    TIME    TIME

   1422.00 1425.44  1.00    0.0
FILE  1 DATA SAVED AT REC NO. 1475
FILE 10 DATA SAVED AT REC NO. 1016



    COMPONENT              TIME         AREA         RESULTS        UNITS
                          (SECS)      (MV-SEC)

   TRIDECANE               234.1        70.961        0.126      WEIGHT%
   TETRADECANE             291.0       407.499        0.721      WEIGHT%
   PENTADECANE             350.6      1175.242        2.080      WEIGHT%
   HEXADECANE              410.9      1715.803        3.037
   HEPTADECANE             469.9      2353.428        4.165
   OCTADECANE              527.5      2514.090        4.450
   NONADECANE              582.4      2746.255        4.861
   EICOSANE                635.7      2974.175        5.264
   HENICOSANE              686.6      3306.405        5.852
   DOCOSANE                734.9      3574.879        6.327
   TRICOSANE               781.2      4089.936        7.239
   TETRACOSANE             825.8      4178.492        7.395
   PENTACOSANE             868.1      4419.819        7.823
   HEXACOSANE              909.1      4431.568        7.843
   HEPTACOSANE             948.7      4595.598        8.134
   OCTACOSANE              987.3      3686.622        6.525
   NONACOSANE             1024.3      3300.198        5.841
```

APPENDIX I - page 2

TRIACONTANE	1059.9	2338.445	4.139	
HENTRIACONTANE	1094.6	1744.546	3.088	
DOTRIACONTANE	1127.9	1160.015	2.053	
TRITRIACONTANE	1162.2	697.509	1.235	
TETRATRIACONTANE	1193.1	408.812	0.724	
PENTATRIACONTANE	1224.1	258.699	0.458	
HEXATRIACONTANE	1256.6	172.011	0.304	
HEPTATRIACONTANE	1292.5	102.740	0.182	
OCTATRIACONTANE	1332.0	77.494	0.137	
C40	1425.4	2291.532	0.000	
	1488.3	19.623		
		------------	-------	
TOTAL		58812.330	100.013	
UNKNOWN	270.1	12.399	0.019	AREA-PERCENT
UNKNOWN	326.0	55.904	0.087	AREA-PERCENT
UNKNOWN	389.3	60.628	0.095	AREA-PERCENT
UNKNOWN	437.2	85.368	0.133	AREA-PERCENT
UNKNOWN	449.9	65.024	0.102	AREA-PERCENT
UNKNOWN	496.8	30.933	0.048	AREA-PERCENT
UNKNOWN	508.1	85.325	0.133	AREA-PERCENT
UNKNOWN	564.4	78.412	0.123	AREA-PERCENT
UNKNOWN	607.1	20.986	0.033	AREA-PERCENT
UNKNOWN	618.0	86.650	0.135	AREA-PERCENT
UNKNOWN	670.3	90.609	0.142	AREA-PERCENT
UNKNOWN	707.0	30.482	0.048	AREA-PERCENT
UNKNOWN	719.3	85.984	0.134	AREA-PERCENT
UNKNOWN	755.9	21.938	0.034	AREA-PERCENT
UNKNOWN	765.9	87.519	0.137	AREA-PERCENT
UNKNOWN	811.2	102.204	0.160	AREA-PERCENT
UNKNOWN	854.1	117.621	0.184	AREA-PERCENT
UNKNOWN	885.1	33.770	0.053	AREA-PERCENT
UNKNOWN	896.1	151.119	0.236	AREA-PERCENT
UNKNOWN	925.7	57.874	0.090	AREA-PERCENT
UNKNOWN	936.7	170.039	0.266	AREA-PERCENT
UNKNOWN	965.4	62.857	0.098	AREA-PERCENT
UNKNOWN	975.7	218.190	0.341	AREA-PERCENT
UNKNOWN	1003.0	174.093	0.272	AREA-PERCENT
UNKNOWN	1013.0	215.564	0.337	AREA-PERCENT
UNKNOWN	1048.6	311.739	0.487	AREA-PERCENT
UNKNOWN	1083.9	312.209	0.488	AREA-PERCENT
UNKNOWN	1115.9	340.069	0.532	AREA-PERCENT

APPENDIX L

PHILLIPS PETROLEUM COMPANY - METHOD 7305-AG

APPENDIX I - Page 3

UNKNOWN	1150.2	307.489	0.481	AREA-PERCENT
UNKNOWN	1181.6	295.691	0.462	AREA-PERCENT
UNKNOWN	1212.6	230.509	0.360	AREA-PERCENT
UNKNOWN	1244.6	197.080	0.308	AREA-PERCENT
UNKNOWN	1278.0	132.707	0.207	AREA-PERCENT
UNKNOWN	1317.0	56.517	0.088	AREA-PERCENT
UNKNOWN	1346.0	190.851	0.298	AREA-PERCENT
UNKNOWN	1376.4	226.404	0.354	AREA-PERCENT
UNKNOWN	1389.9	159.617	0.249	AREA-PERCENT
UNKNOWN	1508.3	103.068	0.161	AREA-PERCENT
UNKNOWN	1557.3	56.804	0.089	AREA-PERCENT
UNKNOWN	1562.2	44.716	0.070	AREA-PERCENT
		------------	-------	
TOTAL		5166.975	8.076	

APPENDIX I - Page 4

1-61F HJ-20246-1-61F GLC# 721366 DATE- 4/ 4/72ANALYST- COJ

CARBON ATOMS PER MOLECULE	MOLE PERCENT	WEIGHT PERCENT	SMOOTHED WEIGHT PERCENTAGES	OEP
13	0.222	0.126		
14	1.185	0.721		
15	3.192	2.080	1.987	1.115
16	4.371	3.036	3.023	1.067
17	5.646	4.165	3.867	1.066
18	5.699	4.449	4.443	1.031
19	5.900	4.860	4.877	1.008
20	6.073	5.263	5.325	1.011
21	6.432	5.851	5.848	1.018
22	6.640	6.326	6.436	1.034
23	7.268	7.238	6.999	1.040
24	7.118	7.394	7.423	1.029
25	7.230	7.822	7.703	1.022
26	6.972	7.842	7.799	1.046
27	6.963	8.133	7.495	1.086
28	5.387	6.524	6.688	1.093
29	4.657	5.840	5.557	1.084
30	3.190	4.138	4.320	1.068
31	2.304	3.087	3.148	1.033
32	1.484	2.053	2.154	1.006
33	0.865	1.234	1.379	0.986
34	0.492	0.723	0.842	1.010
35	0.303	0.458	0.517	1.012
36	0.196	0.304	0.328	0.952
37	0.114	0.182		
38	0.083	0.137		

AVERAGE OEP BETWEEN C-25 AND C-33 IS 1.047 .

APPENDIX L

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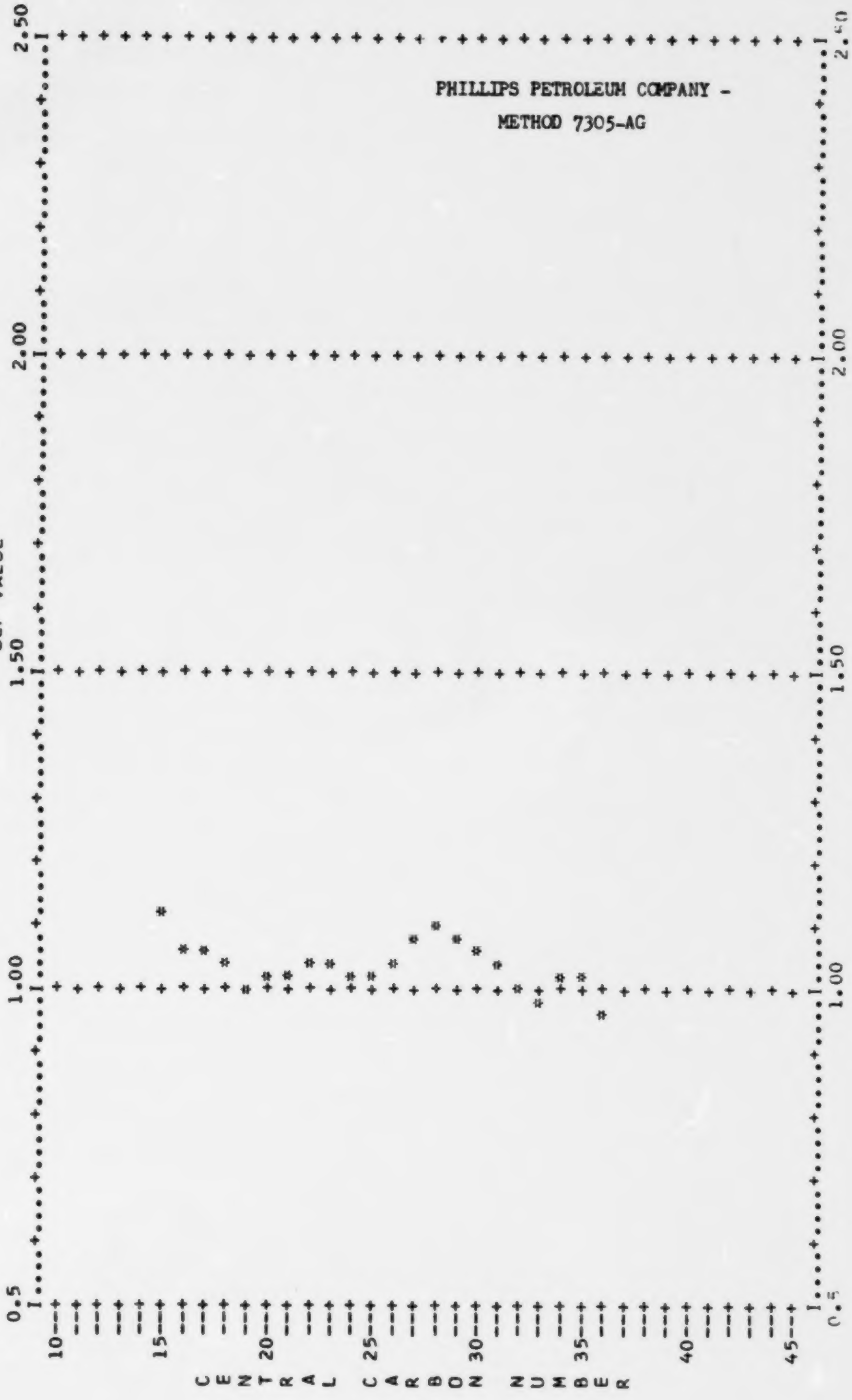
1-61F HJ-20246-1-61F GLC# 721366 DATE- 4/ 4/72ANALYST- COJ



APPENDIX L

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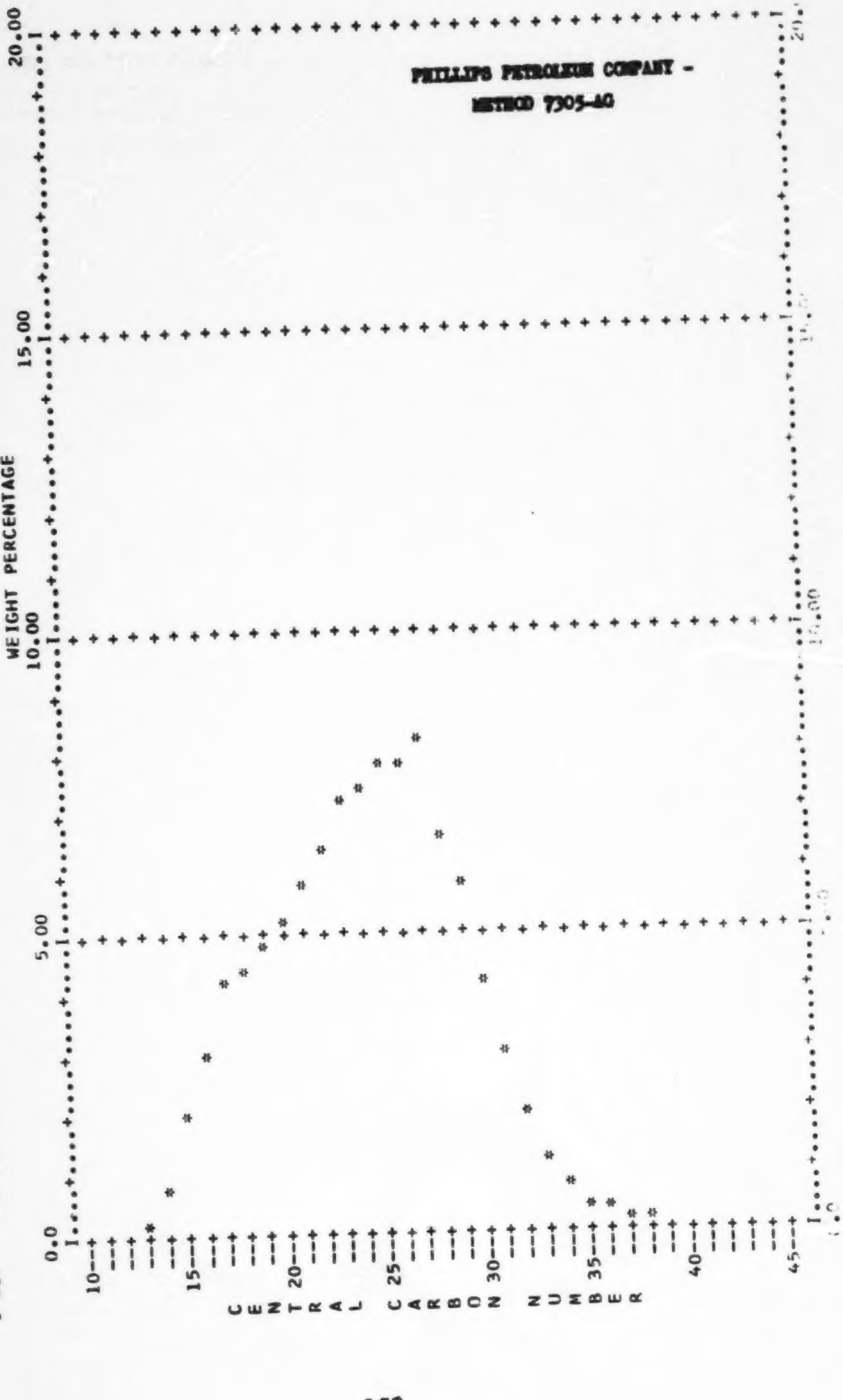
1-61F HJ-20246-1-61F GLC# 721366 DATE- 4/ 4/72ANALYST- COJ

PHILLIPS PETROLEUM COMPANY -
METHOD 7305-AG



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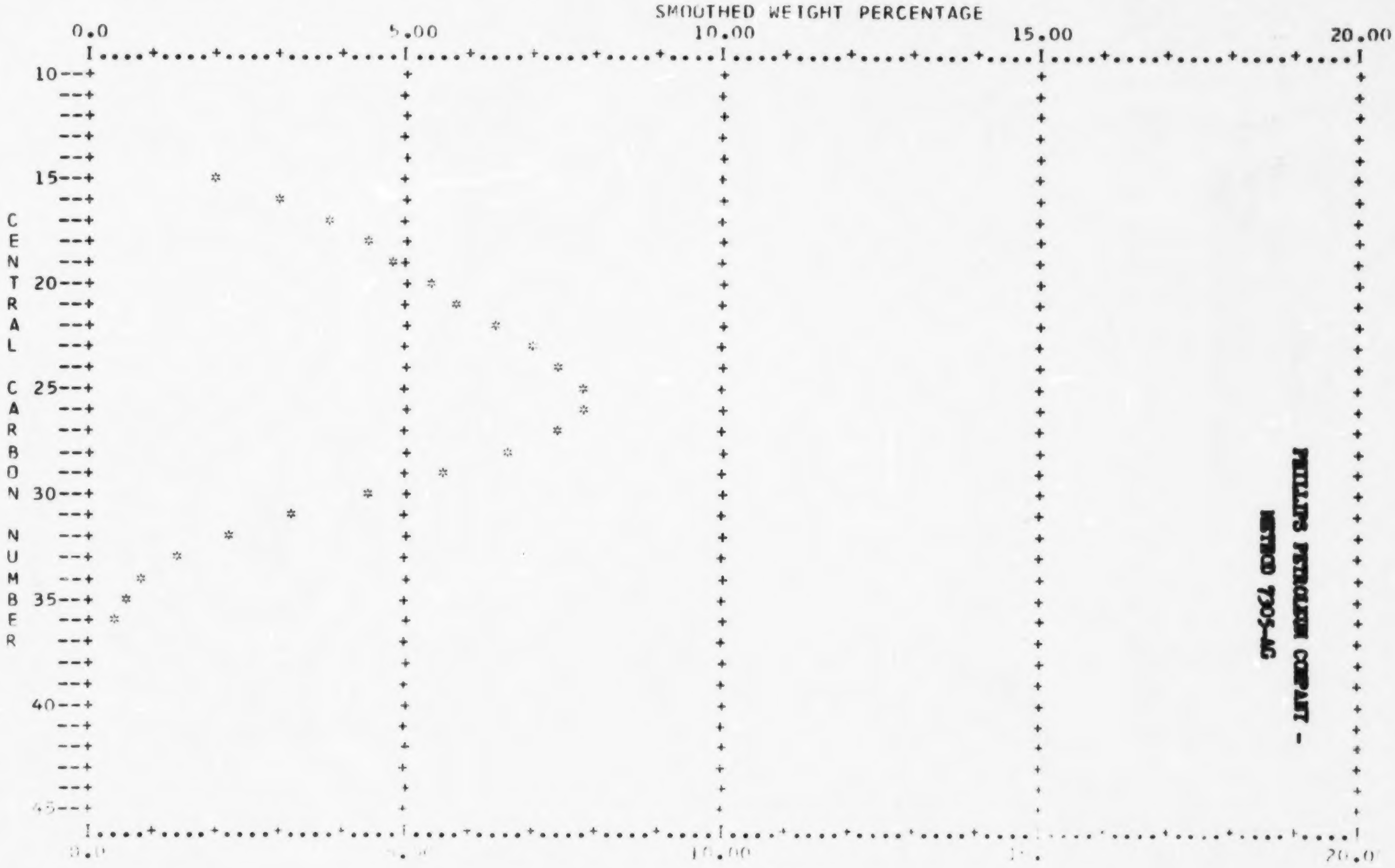

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APPENDIX M

PUBLISHED SULFUR ISOTOPE DATA

Location, Description	% S	$\delta^{34}S$	Reference*
United States			
California			
Summerland 64075	.23	-7.9	a
Wilmington 66096	2.51	+6.8	a
Wilmington	-	8.8	c
Kansas			
Cherokee Penna.	.24	+3.9	d
Louisiana			
Timbalier Bay (Offshore)	-	-6.4	c
Montana			
Woodrow PC 58-399	.90	-4.8	b
Oklahoma			
Konawa-Dora 67074	.44	+2.5	a
Sho-Vel-Tum 59171	1.44	+14.5	a
Springer Penna	.27	-.1	d
Misener Penna	.1	-5.6	d
Texas			
Ellenburger, Ordovician	-	7.8	d
Silurian Silurian	-	+7.7	d
McElroy Permian	-	-2.4	d
Keystone Permian	-	+4.5	d
East Texas Field	-	-5.7	c
Ward Estes, N. Texas	-	.6	c
Goldsmith	-	4.6	c
Kelley Snyder	-	0	c
Sprayberry (Trend Area)	-	1.2	c
Headlee	-	.6	c
Utah			
Red Wash 67131	.31	+12.8	a
Chevron Red Wash	.2	+16.0	a
Green River Eocene	.1	28.2	d

*References on Page 166, Appendix M.

APPENDIX M (Cont'd)

Location, Description	% S	$\delta^{34}S$	Reference*
Wyoming			
River Bend PC 66-39	2.52	-6.6	a
Cowley PC 67-75	3.25	+6.9	a
Reno PC 66-48	.77	-4.5	a
Amoco Reno Crude	-	-4.8	a
Middle Dome PC 67-76	2.58	+5.1	a
Beaver Creek PC 67-73	.54	-2.5	a
Amoco Beaver Crude	-	-3.3	a
Phosphoria, Permian	2.8	-2.9	d
Tensleep, Penna	2.4	-5.1	d
Madison, Miss	1.9	-3.9	d
Lakota Cretaceous	.25	-2.2	d
Frontier Cretaceous	.1	-1.8	d
Wind River Basin			
Paleozoic 8,600 ft	-	-7.6 to -1.7	f
10,000 ft	-	-.6 to +7.5	f
Cretaceous	-	-1 to -3	f
Triassic	-	+2.5	f
Canada			
Alberta			
Leduc Oil Field, Devonian D-2	.3	+12.1	d
Stettler "	1.45	13.1	d
Big Valley "	1.04	12.8	d
Normandville "	.20	10.1	d
Fort Norman, N.W. Terr. "	.33	10.1	d
Excelsior "	.67	15.2	d
Stettler Devonian D-3	1.77	10.8	d
Big Valley "	.63	11.7	d
Bashaw "	.62	13.2	d
Redwater "	.49	10.2	d
Leduc "	.27	12.5	d
Wizard Lake "	.29	15.5	d
Golden Spike "	.19	15.1	d
Bonneyville, Lower Cretaceous	3.9	+7.5	d
Lloydminster "	3.6	6.0	d
Abasand Quarry "	5.0	5.7	d
Taber "	1.7	7.5	d
Brooks Bantry, Blairmore	2.2	5.7	d
Campbell Basal Cretaceous	.87	10.3	d
Whitemud "	.59	11.0	d
Woodbend "	.38	12.0	d
Malmo Lower Cretaceous	.50	10.1	d

APPENDIX M (Cont'd)

Location, Description	% S	$\delta^{34}S$	Reference*
Western Canada			
Joseph Lake, Upper Cretaceous	.13	-1.0	d
Armena "	.14	-1.0	d
Bulwark	.17	-3.0	d
Camrose	.13	-4.1	d
Pembina	.19	-5.2	d
Florence, Sask. Mississippian	.51	+1.3	d
North Steelman	.55	2.3	d
Carnduff	.55	1.9	d
Forget	1.85	6.8	d
Stoughton	2.2	6.3	d
Edenuale	.86	3.6	d
Florence	1.77	3.4	d
Coleville	2.6	4.9	d
Turner Valley	.3	8.8	d
Ontario			
Sombra Silurian	1.0	+9.2	d
West Becher Silurian	.85	+8.4	d
Trenton Ordovician	.1	+6.3	d
Norfolk Silurian	.1	+9.7	d
Canada			
Saskatchewan			
High Prairie Field	-	+9.4	g
Stoughton	-	+9.0	g
Pierson	-	+3.8	g
South America			
Venezuela			
Lagunillas 57124	2.12	+5.2	a
Boscan 59190	5.53	+5.6	a
Lake Marecailo, Ceuta	-	+6.1	c
Columbia			
Orito, Putumayo Basin	-	-4.2	c
Middle East			
American Oil YSN 6796A (Middle East)	2.5	-7.1	a
6796B (Middle East)	1.4	+3.2	a
Iran			
Agha Jari	-	+ .4	c

APPENDIX M (Cont'd)

Location, Description	% S	$\delta^{34}S$	Reference*
Northern Iraq			
Ain Zalah Field, Late Cretaceous	-	-3.2	e
Ain Zalah Field, Middle Cretaceous	-	-2.8	e
Butmah Field, Late Cretaceous	-	-5.3	e
Late Triassic	-	+1.9	
Alan Field, Late Triassic	-	+2.8	e
Demir Dagh Field, Late Cretaceous	-	-6.4	
Kirkuk-Thurmala,-Avanah,-Baba Fields			
Tertiary	-	-5.5	e
Late Cretaceous	-	-5.3	e
Middle Cretaceous	-	-5.5	e
Early Cretaceous	-	-5.9	e
Qarah Cheng Field, Early Cretaceous	-	-3.9	e
Bai Hassan Field, Tertiary	-	-7.1	e
Late Cretaceous	-	-7.0	e
Middle Cretaceous	-	-7.4	e
Early Cretaceous	-	-7.5	e
Jambur Field, Tertiary	-	-6.5	e
Early Cretaceous	-	-4.0	e
Pulkhana Field, Late Cretaceous	-	-5.9	e
Gilabet Field, Tertiary	-	-3.4	e
Kuwait			
Wafra 67065	3.91	-9.8	a
Neutral Zone	-	-8.1	c
Neutral Zone	-	-9.8	c
Neutral Zone	-	-9.7	c
Libya			
Saru, Sule Basin		.3	c
Saudi Arabia			
Ghawar, Ain Dar 57007	1.69	-2.1	a
Ghawar, Haradh 57005	2.14	-1.9	a
Kharsaniya 57002	2.49	-1.6	a
Safaniya 67006	2.97	-8.5	a
Ghawar Blend	-	-1.8	c
United Arab Republic			
El Morgan	-	+2.9	c
Far East			
Sumatra			
Menas	-	- .1	c
Duri	-	- .5	c

APPENDIX M

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APPENDIX N

STATISTICAL PROCEDURE

Introduction

Identifying an unknown oil source falls into the category of a classification problem. It is assumed that there are a finite number of crude oil sources from which the unknown oil may have come and each of these crude oil sources is characterized by a probability distribution of the measured parameters. The unknown oil is considered as a random observation from the known population of crude oils.

The classification problem may be considered as one of "statistical decision functions". We have eighty hypotheses: each hypothesis is that the distribution of the measured parameters for an unknown oil is the same as the distribution of these measured parameters for each known oil. Our procedure must test each of these hypotheses and accept one and reject all the others.

Procedure

The procedure classifies a multivariate x (vector of m measured properties pertaining to the unknown oil) into population k if:

$$q_i p_i(\underset{\sim}{x}) < q_k p_k(\underset{\sim}{x}) \qquad (1)$$

for all $j \neq k$.

In this inequality the q's are a priori probabilities and the $p(\underset{\sim}{x})$'s are multivariate normal density functions. For this problem the q's are assumed equal, i.e., the probabilities are equal that an unknown oil could have come from any one of the oils cataloged in the source library. Also the probability must be unity that an unknown oil did come from one of the sources in the library.

The type of data required for the analysis presented is shown in Table 1, n is the number of oils in the library, m is the number of parameters measured on each oil, and n1, n2,..., nn are the number of replicated samples taken from each crude oil source. The number of replicates for each oil must be greater than or equal to m in order that each of the covariance matrices be non-singular.

In this case the crude oil library consists of 80 (n) oils. Each crude oil is of known source and is characterized by the measured parameters. However, only estimates of the means ($\bar{x}$) and variances ($\hat{\sigma}^2$) for these measured parameters are available for each crude oil source. This restriction results in covariance matrices whose estimates of covariance are zero, i.e., it requires the assumption that the components of the vector $\underset{\sim}{x}$ be uncorrelated for the oil population. This assumption is not unrealistic if oil within a source is homogeneous.

The procedure also assumes that the means for each oil population are different, but that their covariance matrices are alike. For this identification problem, this assumption can not be made, because for sulfur, vanadium and nickel contents the variances depend on the magnitude of these parameters. These variances can be made homogeneous by transforming these variables, but the resulting transformed variables will not have a normal distribution. There is no clear cut way to get around this problem. The identification procedure does require that the variables be distributed normal and have homogeneous variances. If a decision making process is

APPENDIX N

TABLE 1

DATA REQUIRED FOR CLASSIFICATION ANALYSIS

OIL	MEASURED PROPERTIES AND CHARACTERISTICS OF THE OIL					
1	$x^{(1)}_{1,1}$	$x^{(1)}_{2,1}$	$x^{(1)}_{3,1}$	. . .	$x^{(1)}_{m,1}$	
	$x^{(1)}_{1,2}$	$x^{(1)}_{2,2}$	$x^{(1)}_{3,2}$	. . .	$x^{(1)}_{m,2}$	
	.	.	.		.	
	.	.	.		.	
	.	.	.		.	
	$x^{(1)}_{1,n1}$	$x^{(1)}_{2,n1}$	$x^{(1)}_{3,n1}$	. . .	$x^{(1)}_{m,n1}$	$n1 \geqslant m$
2	$x^{(2)}_{1,1}$	$x^{(2)}_{2,1}$	$x^{(2)}_{3,1}$	. . .	$x^{(2)}_{m,1}$	
	$x^{(2)}_{1,2}$	$x^{(2)}_{2,2}$	$x^{(2)}_{3,2}$	. . .	$x^{(2)}_{m,2}$	
	.	.	.		.	
	.	.	.		.	
	.	.	.		.	
	$x^{(2)}_{1,n2}$	$x^{(2)}_{2,n2}$	$x^{(2)}_{3,n2}$	. . .	$x^{(2)}_{m,n2}$	$n2 \geqslant m$
.						
.						
.						
n	$x^{(n)}_{1,1}$	$x^{(n)}_{2,1}$	$x^{(n)}_{3,1}$	. . .	$x^{(n)}_{m,1}$	
	$x^{(n)}_{1,2}$	$x^{(n)}_{2,2}$	$x^{(n)}_{3,2}$	. . .	$x^{(n)}_{m,2}$	
	.	.	.		.	
	.	.	.		.	
	.	.	.		.	
	$x^{(n)}_{1,nn}$	$x^{(n)}_{2,nn}$	$x^{(n)}_{3,nn}$	. . .	$x^{(n)}_{m,nn}$	$nn \geqslant m$

incorporated into the identification procedure that will reduce the total number of potential crude oil sources down to three: the major candidate and its two nearest competitors, then the ranges of the measured parameters will be narrowed down to the point, where for all practical purposes, their variance estimates can be assumed to be the same. This process greatly reduces the size of the problem and the complications involved in determining the probabilities of misclassification.

Initially the 80 crude oils were characterized by measured parameters. It has been demonstrated that 6 (m) parameters are sufficient to discriminate among crude oils sources given in the data library. These six parameters measured on the 600+F bottoms are:

$$\left.\begin{array}{ll} \text{1. Sulfur, Wt. \%} & =x_1 \\ \text{2. Nitrogen, Wt. \%} & =x_2 \\ \text{3. Vanadium, ppm} & =x_3 \\ \text{4. Nickel, ppm} & =x_4 \\ \text{5. Carbon isotopic ratio, 600+F} & =x_5 \\ \text{6. Sulfur isotopic ratio, 600+F} & =x_6 \end{array}\right\} = \underset{\sim}{x}$$

Given the values for these six parameters, an unknown oil can be classified into its most probable source and its two primary competitors determined.

Table 2 gives the multivariate normal density function for population i. It also shows the reduction of this function when the covariance matrix ($\Sigma^{(i)}$) is diagonal.

The inequality (1) can be reduced to the expression

$$p_j(\underset{\sim}{x}) < p_k(\underset{\sim}{x}) \quad , \text{ for all } j \neq k, \tag{2}$$

TABLE 2

MULTIVARIATE NORMAL DENSITY FUNCTION FOR POPULATION i

$$P_i(\underset{\sim}{x}) = \frac{1}{(2\pi)^{6/2}\,|\Sigma^{(i)}|^{1/2}}\ \mathrm{EXP}\,[-1/2\,(\underset{\sim}{x}-\underset{\sim}{\mu}^{(i)})'\,\Sigma^{(i)^{-1}}\,(\underset{\sim}{x}-\underset{\sim}{\mu}^{(i)})].$$

COVARIANCE MATRIX

$$\Sigma^{(i)} = \begin{pmatrix} (\sigma_1{}^{(i)})^2 & & & & & \phi \\ & (\sigma_2{}^{(i)})^2 & & & & \\ & & (\sigma_3{}^{(i)})^2 & & & \\ & & & (\sigma_4{}^{(i)})^2 & & \\ & & & & (\sigma_5{}^{(i)})^2 & \\ \phi & & & & & (\sigma_6{}^{(i)})^2 \end{pmatrix} = D^{(i)}\ \text{(DIAGONAL)}$$

6X6 MATRIX

REDUCED DENSITY FUNCTION WHEN COVARIANCE MATRIX IS DIAGONAL

$$P_i(\underset{\sim}{x}) = \frac{1}{(2\pi)^3 \prod_{j=1}^{6} \sigma_j{}^{(i)}}\ \mathrm{EXP}\,[-1/2\sum_{j=1} \left(\frac{x_j-\mu_j^{(i)}}{\sigma_j{}^{(i)}}\right)^2]$$

$\underset{\sim}{x}$ = 6X1 VECTOR OF MEASURED PROPERTIES

$\underset{\sim}{\mu}^{(i)}$ = 6X1 VECTOR OF MEANS OF MEASURED PROPERTIES FOR POPULATION i.

$(\sigma_j{}^{(i)})^2$ AND $\sigma_j{}^{(i)}$ = VARIANCES AND STANDARD DEVIATIONS OF THE SIX MEASURED PROPERTIES FOR POPULATION i.

since the a priori probabilities (q's) are assumed equal. Substituting the density functions into this expression gives:

$$\frac{1}{(2\pi)^3 \prod_{i=1}^{6} \hat{\sigma}_i(j)} \ \text{EXP} \left(-\frac{1}{2} \sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(j)}}{\hat{\sigma}_i(j)} \right)^2 \right) < \frac{1}{(2\pi)^3 \prod_{i=1}^{6} \hat{\sigma}_i(k)} \ \text{EXP} \left(-\frac{1}{2} \sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(k)}}{\hat{\sigma}_i(k)} \right)^2 \right) \tag{3}$$

for all $j \neq k$.

This says to classify the vector of components measured on the unknown oil into the population (source oil) whose density function, when evaluated for $\underset{\sim}{x}$, is largest. This in essence is the population (k) that minimizes the expression:

$$\sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(k)}}{\hat{\sigma}_i(k)} \right)^2 , \tag{4}$$

where $\hat{\mu}^{(k)}$ is an estimate of the mean and $\hat{\sigma}_i(k)$ is an estimate of the standard deviation for variable i of population k. This expression is a portion of the exponential term in the density function. The failure of the variance to be homogeneous among oil sources could conceivably result in different conclusions being drawn from minimizing expression (4) and maximizing the density functions, but the likelihood of this is remote.

The procedure numerically evaluates expression (4) for each of the eighty crude oils given in the data library. The source crude oils are ranked from most likely to least likely that $\underset{\sim}{x}$ could have come from their distribution based on the evaluation. The procedure then takes the oil source that ranks first as the most probable candidate for $\underset{\sim}{x}$ to have come from and the oil sources that rank 2 and 3 as its primary competitors. The density functions for these 3 oil sources are evaluated to confirm that the ranking is correct and not influenced by the failure of variances to be homogeneous.

The assumption of equivilant covariance matrices for the three oil populations determined in the previous step is now reasonable, since the means of each parameter in these 3 crude oils cover a narrower range. An estimate of the covariance matrix that is representative of the 3 populations is obtained by pooling the covariance matrices for the three crude oils.

This covariance matrix is then substituted into expression (3) and the resulting inequality becomes:

$$\frac{1}{(2\pi)^3 \prod_{i=1}^{6} \hat{\sigma}_i} \ \text{EXP} \left(-\frac{1}{2} \sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(j)}}{\hat{\sigma}_i} \right)^2 \right)$$

$$\frac{1}{(2\pi)^3 \prod_{i=1}^{6} \hat{\sigma}_i} \ \text{EXP} \left(-\frac{1}{2} \sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(k)}}{\hat{\sigma}_i} \right)^2 \right), \qquad (5)$$

for all $j \neq k$. The difference between (3) and (5) is that the standard deviations are no longer identified with a particular crude oil source. They are, in fact, the same for the three oil crude sources in question. Expression (5) can be reduced farther by cancelling the constant terms and taking the logarithm of both sides. The expression simplifies to:

$$\sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(j)}}{\hat{\sigma}_i} \right)^2 > \sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(k)}}{\hat{\sigma}_i} \right)^2, \quad \text{for all } j \neq k \qquad (6)$$

APPENDIX N

This says, classify the vector of components $\underset{\sim}{x}$ into population (crude oil source) k when the above inequality is satisfied for all $j \neq k$. In other words, classify $\underset{\sim}{x}$ into the population that yields a minimum value for:

$$\sum_{i=1}^{6} \left(\frac{x_i - \hat{\mu}_i^{(k)}}{\hat{\sigma}_i} \right)^2 . \qquad (7)$$

This is the same criterion used to select the 3 candidate oils. Had the covariance matrix been the same for all eighty crude oil sources, expressions (4) and (7) would have been the same and the solution would be greatly simplified.

Equation (6) may be further simplified:

$$\sum_{i=1}^{6} \left(\frac{x_i \hat{\mu}_i^{(k)} - x_i \mu_i^{(j)}}{\hat{\sigma}_i^2} \right) - \sum_{i=1}^{6} \left(\frac{(\hat{\mu}_i^{(k)})^2 - (\hat{\mu}_i^{(j)})^2}{2 \hat{\sigma}_i^2} \right) > 0. \qquad (8)$$

The left hand side of this inequality is a linear function of normal variables. Therefore, assuming the vector is a sample from crude oil source k, then the variable

$$U_{(kj)} = \sum_{i=1}^{6} \left(\frac{x_i \hat{\mu}_i^{(k)} - x_i \hat{\mu}_i^{(j)}}{\hat{\sigma}_i^2} \right) - \sum_{i=1}^{6} \left(\frac{(\hat{\mu}_i^{(k)})^2 - (\hat{\mu}_i^{(j)})^2}{2 \hat{\sigma}_i^2} \right) \qquad (9)$$

is distributed normal with mean $\frac{1}{2} a_{kj}$ and variance a_{kj},

where:

$$a_{kj} = \sum_{i=1}^{6} \left(\frac{\hat{\mu}_i^{(k)} - \hat{\mu}_i^{(j)}}{\hat{\sigma}_i} \right)^2 . \qquad (10)$$

APPENDIX N

The probability of misclassification is defined as:

Prob. {of not classifying $\underset{\sim}{x}$ in population k, given that $\underset{\sim}{x}$ came from population k}

$$= \text{Prob}\ \{U_{kj} < 0;\ \text{for all } j \neq k\} \tag{11}$$

$$= 1 - \text{Prob}\ \{U_{kj} > 0;\ \text{for all } j \neq k\}$$

Letting $j = 1, 2$ or 3 and evaluating the procedure for $k = 3$ this probability statement becomes:

= Prob {of not classifying $\underset{\sim}{x}$ in pop. 3 given that $\underset{\sim}{x}$ came from pop. 3}

$$= 1 - \text{Prob}\ \{U_{31} > 0,\ U_{32} > 0\} \tag{12}$$

The vector

$$\underset{\sim}{U}_3 = \begin{pmatrix} u_{31} \\ u_{32} \end{pmatrix} \sim \text{BVN}\left(\begin{pmatrix} \frac{1}{2}a_{31} \\ \frac{1}{2}a_{32} \end{pmatrix}, \begin{pmatrix} a_{31} & a_{312} \\ a_{312} & a_{32} \end{pmatrix} \right), \tag{13}$$

where

$$a_{32} = \sum_{i=1}^{6} \left(\frac{\hat{\mu}_i^{(3)} - \hat{\mu}_i^{(1)}}{\hat{\sigma}_i} \right) \left(\frac{\hat{\mu}_i^{(3)} - \hat{\mu}_i^{(2)}}{\hat{\sigma}_i} \right) \tag{14}$$

and the means and variances are defined as above. Since the vector $\underset{\sim}{U}_k$ is distributed as a bivariate normal the Prob $\{U_{31} > 0,\ U_{32}\ 0\}$ =

$$\int_0^\infty \int_0^\infty g\ (U_{31},\ U_{32} : \rho)\ dU_{31}\ dU_{32}, \tag{15}$$

where $g\ (U_{31},\ U_{32} : \rho)$ is the bivariate normal density function. The vector $\underset{\sim}{U}_k$ can be standardized to means 0, variance and correlation ρ, and the value of this probability (15) can be looked up in available bivariate normal tables. The probability of misclassification is 1 minus this value.